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Clare L.S. Wiseman *Editors*

Platinum Metals in the Environment

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Platinum Metals in the Environment

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Foreword

Platinum group elements (PGE) naturally occur at trace concentrations in most surficial environments. Anthropogenic uses and emissions of PGE are now changing the environmental concentrations and biogeochemical cycle of these elements. Automobile catalysts, which were introduced in the 1970s, represent the largest PGE use, and are generally considered as the main source of PGE into the environment. Early PGE research in the 1970s and 1980s showed that PGE emissions from the catalysts caused elevated concentrations of these normally rare metals in the roadside environment. These first findings paved the way for further research, and by the mid-1990s an active research community, mainly in Europe, was investigating the emission and environmental occurrence of Pt, Pd, and Rh. The most important finding at the time was certainly that PGE are bioavailable, raising concern over the potential risks of this new contamination. It is also important to note that PGE research was supported by analytical developments and a clear focus on measurement accuracy. In recent years, PGE research was marked by a new shift. As automobile catalysts are being introduced in developing countries, the PGE research community is broadening and publications from Argentina, Brazil, China, Ghana, Mexico, or South Africa have appeared in the scientific literature. Congested cities and poor vehicle conditions are a new challenge and raise concern over potential PGE levels in the developing world.

Despite decades of active PGE research, many questions remain. Emissions rates from automobile catalysts are still uncertain. Other potential PGE sources have not been characterized in sufficient details. The finding of elevated PGE concentrations at remote sites shows that the geographical extent of PGE contamination is unclear. The physico-chemical forms and transformations of PGE are largely unknown. Further work is needed to assess the mobility and bioavailability of PGE under environmental conditions. Chronic effects on man and the environment are unclear. Answering these questions is key to assessing the potential risks of PGE emissions.

“Platinum Metals in the Environment” is the fourth book on the environmental PGE research published by Springer. I believe the publication of this new book is an important addition to the series. It brings together a wider research community and provides an overview of the latest developments in PGE research. I warmly recommend this book to anyone interested in the PGE and their environmental relevance.

Gothenburg, June 2014 Sebastien Rauch

Preface

Platinum group elements (PGE) are six rare metals, platinum (Pt), palladium (Pd), iridium (Ir), rhodium (Rh), ruthenium (Ru), and osmium (Os), with excellent catalytic properties. Most notably, Pt, Pd, and Rh have been increasingly used in a number of applications over the last three decades. They are employed as catalysts in various chemical processes such as in hydrating and dehydrating reactions in the pharmaceutical industry and in the production of synthetic polymers, pesticides, and dyes. Following the initial introduction of automotive catalytic converters in North America in the 1970s, Pt, Pd, and Rh have been widely used as the catalysts of choice to reduce nitrous oxide, carbon monoxide, and hydrocarbon emissions in fuel exhaust. In fact, the largest application of PGE is the catalytic converter industry, which used 45, 78, and 80 % of the global production (supply + recycling) of Pt, Pd, and Rh in 2013, respectively (Johnson Matthey Platinum 2013, Interim Review).

While the use of automotive catalytic converters have greatly contributed to the improvement of air quality, it has also led to an accumulation of PGE in the environment, as these catalysts are emitted in small amounts due to mechanical, thermal, and chemical stressors. The potential environmental and human health effects of PGE emissions in automotive exhaust have been controversial, and the focus of much debate. In addition to automotive exhaust emissions, chemical facilities and the mining industry are primary emitters of PGE. Despite the solid body of research over the years, which has provided strong evidence regarding the increased presence of PGE in the atmosphere, large gaps in our knowledge regarding the possible environmental health implications of emissions still remain.

While original research on PGE emissions in the environment stems from the 1980s, considerable advancements have been made on this topic in the last 10 years, especially in terms of the development of analytical methodologies. Along with this, has been a rash and welcome increase in the number of studies examining various aspects of PGE emissions to the environment. New data has been generated regarding the chemical behavior of PGE, including their environmental mobility, solubility, bioaccessibility, and toxic potential. This edited volume, “Platinum Metals in the Environment”, builds upon three previously edited books by Zereini and Alt, published by Springer-Verlag: "Emissionen von Platinmetallen: Analytik, Umwelt- und Gesundheitsrelevanz" (1999), "Anthropogenic Platinum-Group Element Emissions—Their Impact on Man and Environment" (2000), and "Palladium Emissions in the Environment: Analytical Methods, Environmental Assessment and Health Effects" (2006). The book compiles the most up-to-date results of interdisciplinary research on the topic of PGE emissions and introduces brand new insights into their chemical speciation, behavior, and potential to impact human health.

The book is grouped into five main parts, each consisting of contributions addressing similar aspects of each of the main topical areas: (1) Sources of PGE Emissions, (2) Analytical Methods for the Determination of PGE in Biological and Environmental Matrices, (3) Occurrence, Chemical Behavior, and Fate of PGE in the Environment, (4) Environmental Bioavailability and Biomonitoring of PGE, and (5) Human Health Exposures to PGE and Possible Risks.

A total of 61 scientists from 14 different countries contributed to this highly interdisciplinary volume, addressing topics covering the fields of chemistry, biology, geochemistry, and medicine. The range of topics covered and the research results presented and discussed will make this book of interest to experts both inside and outside of academia, as well as to post-secondary undergraduate and graduate students.

The editors would like to thank the authors and the reviewers for their timely efforts and valuable contributions to this highly successful, cooperative endeavor. Many thanks go to our colleagues of the Noble Metal Forum in Germany for their support: Prof. Dr. Kerstin Leopold (Institute of Analytical and Bioanalytical Chemistry, University of Ulm, Germany), Prof. Dr. Michael Schuster (Analytical Chemistry, Technische Universität München, Germany), Dr. Rudolf Schierl (Institute and Outpatient Clinic for Occupational, Social and Environmental Medicine, University Hospital of Munich, Germany), Prof. Dr. Stephan Hann (Department of Chemistry, University of Natural Resources and Life Sciences—BOKU Vienna, Austria) and Prof. Dr. Bernd Sures, Dr. Sonja Zimmermann und Dr. Nadine Ruchter (Aquatic Ecology and Centre for Water and Environmental Research, University of Duisburg-Essen, Germany).

In addition, special thanks go to Prof. Dr. Sebastien Rauch (Department of Civil and Environmental Engineering, Chalmers University of Technology, Sweden), Prof. Dr. Rumyana Djingova (Faculty of Chemistry and Parmacy University of Sofia, Bulgaria), Prof Dr. Vojtech Adam (Department of Chemistry and Biochemistry Faculty of Agronomy, Mendel University in Brno, Czech Republic), Prof. Dr. Ana Maria G. Figueiredo (Instituto de Pesquisas Energéticas e Nucleares, São Paulo, Brazil), Prof. Dr. Ivo Iavicoli (Institute of Public Health—Section of Occupational Medicine Università Cattolica del Sacro Cuore, Italy), Prof. Dr. Beata Godlewska-Żyłkiewicz (University of Bialystok, Institute of Chemistry, Poland), Prof. Dr. Krystyna Pyrzynska (Warsaw University, Chemistry Dept. Laboratory of Flow Analysis and Chromatography, Warsaw, Poland), Prof. Dr. Shankararaman Chellam (Department of Civil and Environmental Engineering, University of

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We would like to express our gratitude to Springer-Verlag for making this book publication possible. In particular, we are grateful to Agata Oelschläger for her editorial expertise and assistance. Finally, we would like to extend our thanks to our families for their patience, understanding, and support.

Frankfurt am Main, Germany, June 2014 Fathi Zereini
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Part I
Sources of PGE Emissions

Sources of Platinum Group Elements in the Environment

Sebastien Rauch and Bernhard Peucker-Ehrenbrink

Abstract Platinum group elements (PGE, i.e. Pt, Pd, Rh, Ir, Ru, Os) are among the least abundant elements in the Earth's continental crust. PGE concentrations in urban and roadside environments are, however, increasing as a result of anthropogenic emissions. Automobile catalysts are generally considered the main PGE source into the urban and roadside environments. We argue that most studies to date have been carried out with a presumption of potential sources, and this bias may have masked additional, yet unidentified PGE sources. Comparison of environmental records at urban locations suggests that PGE emissions reflect contributions from several sources, including automobile catalysts, industry and medical treatment centers. Coal combustion may also contribute to urban PGE fluxes. Environmental records at remote locations support contributions from such diverse sources. Estimates of PGE emissions, however uncertain, indicate that these diverse sources contribute significantly to the global PGE budget at the Earth's surface.

1 Introduction

The highly siderophile properties of the platinum group elements (PGE, i.e. Pt, Pd, Rh, Ir, Os, Ru) has caused segregation of the vast majority of these elements' terrestrial inventories into the Earth's core (Goldschmidt 1922). Consequently, PGE are among the most depleted elements in the Earth's crust relative to bulk earth abundances (Noddack and Noddack 1931; Wedepohl 1995; Peucker-Ehrenbrink and Jahn 2001). The natural biogeochemical cycles of these elements at the Earth's

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surface are dominated by erosion of the continental crust, volcanic eruptions and accretion of extraterrestrial matter. The low natural backgrounds facilitate the detection of even small anthropogenic additions to the natural PGE cycles in the Critical Zone. Increasing use of PGE in a range of applications is now resulting in the release of PGE into the environment to an extent that anthropogenic PGE fluxes are exceeding natural fluxes at the Earth's surface (Klee and Graedel 2004; Sen and Peucker-Ehrenbrink 2012).

Anthropogenic emissions have largely been attributed to automobile exhaust catalysts, which use Pt, Pd and Rh as main active component for the removal of harmful gases (i.e. CO, NOx and hydrocarbons) from automobile exhaust fumes. The introduction of automobile catalysts in the USA in the mid-1970s and in Europe in the 1980 s led to investigations on PGE emissions (e.g. König et al. 1992; Palacios et al. 2000; Moldovan et al. 2002) and their accumulation in urban and roadside environments (e.g. Ely et al. 2001; Gomez 2002; Rauch et al. 2004, 2006; Zereini et al. 2004). Other documented anthropogenic PGE sources are metal production (Niskavaara et al. 2004; Rodushkin et al. 2007; Rauch and Fatoki 2013) and medical applications (Esser and Turekian 1993; Kummerer et al. 1999). PGE also enter waste streams through their uses and emissions, making wastes and sewage additional PGE sources into the environment (Ravizza and Bothner 1996; Lashka and Nachtwey 2000). Recent studies performed in remote environments suggest that additional anthropogenic sources contribute to the PGE cycles in surface environments (Rauch et al. 2010; Sen et al. 2013).

This chapter critically reviews current knowledge of PGE sources and raises questions over the completeness of this knowledge. We argue that most studies to date have been carried out with a presumption of relevant, well-documented sources. This bias may have masked additional, yet unidentified PGE sources.

2 Automobile Catalysts as a Source of PGE

Automobile catalysts are devices placed in the exhaust system of vehicles to convert gaseous pollutants (i.e. carbon monoxide, nitrogen oxides and hydrocarbons) emitted from the engine into less hazardous forms. The catalysts use Pt, Pd and Rh as main active components and are the most potent PGE source owing to the amount of PGE used (37, 72 and 79 % of Pt, Pd and Rh demand, respectively) (Fig. 1) and the usage pattern (exhaust gas flowing through a PGE containing matrix).

PGE emissions from catalysts during vehicle operation have been documented in both bench tests and environmental studies. Emissions are thought to result from mechanical abrasion and chemical reactions at the catalyst surface (Moldovan et al. 2003). Emission rates measured in bench tests are in the ng km^{-1} range (König et al. 1992; Palacios et al. 2000; Moldovan et al. 2002). Emission rates are significantly higher for diesel catalysts than for three-way catalysts used with gasoline engines (Moldovan et al. 2002), and at higher speeds (König et al. 1992). Emission

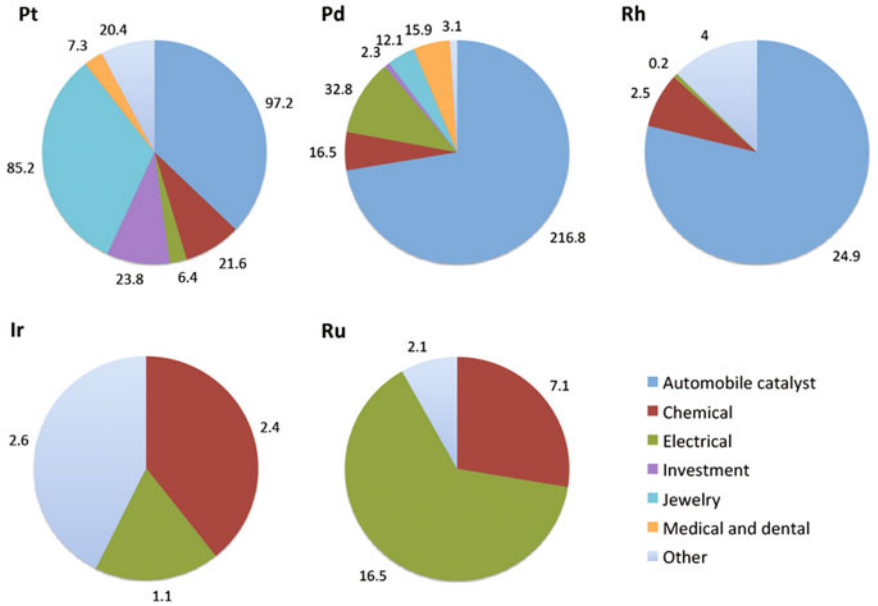

Fig. 1 Estimates of Pt, Pd, Rh, Ir and Ru demands in metric tons in different applications in 2013. Chemical applications include petrochemical and electrochemical uses. *Data source* Matthey (2013)

rates reported by Moldovan et al. (2002) and measured using a driving cycle representing both urban and non-urban driving conditions with speeds up to 120 km h^{-1} are summarized in Table 1. The emission rate inferred from Pt deposition at an urban site is similar to measured emission rates for gasoline catalysts (Lashka et al. 1996). The average relatively low speed (50 km h^{-1}) at this site may, however, have affected the results, and a higher emission rate can be expected for non-urban driving conditions (Helmers and Kummerer 1999). In addition, Helmers (1997) suggests that emissions might also be enhanced by engine malfunction (e.g. ignition problems), and estimates emission rates of the order of 0.5–0.8 μg Pt km^{-1}. Such high emission rates are supported by estimates of Pt losses during a vehicle's lifetime, putting an upper limit on emission rates at 10 μg km^{-1} (40 % Pt loss for a mileage of 100,000 km) (Helmers 1997). Using an emission rate of 0.1–0.8 μg Pt km^{-1}, Rauch et al. (2005b) estimated that 0.8–6.0 metric tons of Pt are emitted annually by automobile catalysts. Based on the emission range shown in Table 1, we extend the emission range to 0.01–6.0 tons Pt $year^{-1}$. As most vehicles equipped with a catalyst are operated in the Northern Hemisphere, this flux is expected to be representative of the global Pt emission. It is important to note that estimates of PGE emission from automobile catalysts remain quite uncertain despite nearly 30 years of research.

Table 1 Estimates of PGE emission rates from automobile catalysts

Estimation	Catalyst	Emission rates (ng km^{-1})			References
		Pt	Pd	Rh	
Direct measurements, exhaust samples collected on bench test with driving cycle representing both urban and non-urban driving conditions, catalyst mileage 30,000 km	Pt-Pd-Rh (gasoline)	6.3	12.0	3.7	Moldovan et al. (2002)
	Pd-Rh (gasoline)	8.2	15.9	12.2	Moldovan et al. (2002)
	Pt (diesel)	152	46	26	Moldovan et al. (2002)
	Pt (diesel)	110	82	39	Moldovan et al. (2002)
Inferred from deposition at an urban site, speed 50 km h^{-1}	–	5	–	–	Lashka et al. (1996)
Inferred from emission estimates for different vehicle and driving conditions, and comparison with environmental samples	–	500–800	–	–	Helmers (1997)

Although Pt, Pd and Rh are the main active ingredients of automobile catalytic converters, Os has been reported to be present as an impurity in such catalysts (Poirier and Gariepy 2005). Environmental studies suggest that Ir and Ru are also present as impurities (Fritsche and Meisel 2004; Rauch et al. 2004). Automobile catalysts are therefore also considered to be sources of Os, Ir and Ru to the environment.

3 Are Automobile the Main Source of PGE in Urban Areas?

The introduction of automobile catalysts and initial reports of PGE emissions from such catalysts raised concern over the potential risks of this new contamination. Several studies aimed at assessing PGE levels in urban and roadside environments and have shown that PGE concentrations are elevated relative to expected natural concentrations or concentrations in remote environments. These studies have also attempted to confirm an automobile catalyst source through various strategies, including sampling at sites with varying traffic intensities (Gomez 2002; Rauch et al. 2006), sampling at increasing distances from automobile traffic (Helmers 1996; Zereini et al. 2000; Jarvis et al. 2001; Ely et al. 2001), estimation of temporal changes in PGE concentrations or accumulation rates (Rauch et al. 2004, 2006), the use of PGE ratios (Ely et al. 2001; Gomez 2002; Rauch et al. 2005a, 2006) as well as correlations with other elements presents in catalysts (Helmers 1996; Rauch et al. 2000). More recently, the isotopic composition of Os (^{187}Os/^{188}Os) has shown that elevated PGE concentrations in urban air are associated with unradiogenic (i.e. low ^{187}Os/^{188}Os values) PGE sources in urban environments (Rauch et al. 2005a, 2006) that are similar to the Os isotopic composition of catalysts (Poirier and Gariepy 2005).

While many studies support an automobile catalyst source, these studies also present discrepancies. For instance, relatively small differences have been reported between cities with different population sizes, vehicle numbers and catalyst introduction dates, as well as traffic patterns and intensities at specific sampling locations. Pt concentrations in airborne particles range from 3.9 to 15.6 pg m^{-3} in six cities in Western Europe (Gomez 2002). For comparison, Pt concentrations of 6.9 ± 1.9 and 9.6 ± 1.8 pg m^{-3} were reported for airborne particles in Boston, USA (Rauch et al. 2005a) and Mexico City, Mexico (Rauch et al. 2006), respectively. PGE concentrations do not necessarily correlated with traffic intensities. For instance, relatively high PGE concentrations at a site with low traffic intensity in Mexico City were attributed to an industrial source (Rauch et al. 2006). In addition, no significant difference was found between airborne PGE concentrations in samples collected on weekdays and weekends in Boston, USA, although traffic intensity is expected to be lower on weekends (Rauch et al. 2005a). PGE abundance ratios in environmental samples, which were used to confirm an automobile catalyst source in some studies, do not necessarily match expected catalyst compositions (Fig. 2). In addition, abundance ratios in catalysts are not always measured, and their use is therefore not necessarily valid. For instance, different PGE ratios between Hong Kong and Mainland China have been attributed to differences in automobile catalyst composition, although automobile catalyst compositions have not been documented (Qi et al. 2011).

Discrepancies between expected and observed PGE concentrations or abundance ratios suggest that a number of sources contribute to PGE fluxes in urban areas. Contributions from other sources are supported by studies of PGE at water treatment plants, which collect water from urban areas and therefore integrate emissions from different sources. A Pt flux of 5.3 kg yr^{-1} has been estimated for a wastewater

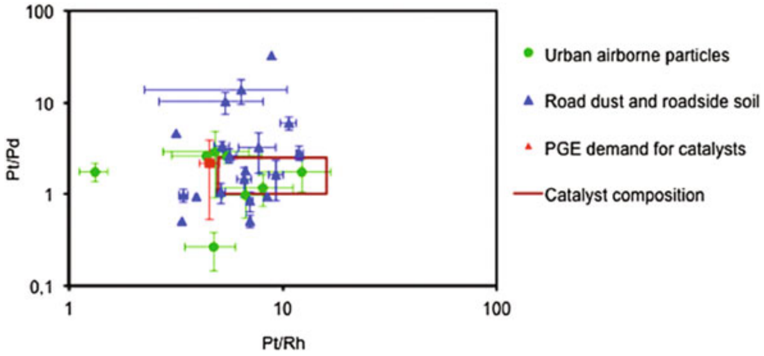

Fig. 2 Comparison of published PGE ratios (Pt/Pd vs. Pt/Rh) in road dust and roadside soils obtained in urban and roadside environments (data published in Rauch et al. 2005b) with automobile catalyst composition (Ely et al. 2001) and PGE demand for catalysts (Johnson Matthey)

treatment plant in Munich, Germany, that includes 0.9 kg yr^{-1} from automobile catalyst emissions (Lashka and Nachtwey 2000). In contrast, another study indicates that automobile catalysts are the main source of PGE in sewage sludge in the UK, although elevated Pd concentrations at three sites could not be attributed to an automobile catalyst source (Jackson et al. 2010). This difference supports the contention that there is no dominant PGE source that explains findings in all urban areas. The relative importance of different PGE sources therefore depends on specific characteristics of an urban area.

4 PGE Emissions from Non-automobile Sources

Studies of the occurrence of PGE in urban settings suggest that multiple sources contribute to anthropogenic PGE fluxes. In this section, we assess the relevance of documented non-automobile PGE sources that may contribute to both local and global PGE cycles, including PGE production activities, industry and medical applications.

4.1 PGE Uses as Indicator for PGE Sources

PGE are used in a range of applications besides automobile catalysts (Fig. 1). Jewelry is an important use for Pt (33 % of Pt demand), but very high recycling rates make this use an unlikely source of significant Pt emissions into the environment. Although other uses are more limited, they may contribute significantly to PGE releases into the environment. The use of Pt-based drugs in cancer treatment that accounts for about 5 % of total Pt demand may cause the emission of this metal into the environment through the excretion of administered drugs. Electrical applications, uses by the chemical industry, jewelry and dental applications are unlikely to be significant sources of PGE into the environment. Therefore, significant Ir and Ru emissions are unlikely. Osmium has a limited number of uses, the largest single use being as fixative and stain in the preparation of tissue thin sections for optical and electron microscopy (Esser and Turekian 1993). It should, however, be noted that PGE uses may contribute to elevated PGE loadings in waste and sewage streams despite active recycling of automobile catalysts and electronic components.

4.2 PGE Emissions from Mining and Production Activities

PGE mining and production activities in South Africa and Russia have been reported to cause emission of PGE into the environment. Elevated Pt concentrations were found near Pt mining and ore processing sites in the Bushveld Igneous

Complex, South Africa. The highest concentration in soils (i.e. 653 ng g^{-1}) was measured near a PGE smelter (Rauch and Fatoki 2013). Nickel, Cu and PGE production in Northern Europe has also been implicated in PGE emissions. Nickel smelters on the Kola Peninsula in NW Russia have been identified as important regional sources of Pt and Pd based on the spatial distribution of these metals in environmental samples (Niskavaara et al. 2004). In addition, chromium smelters in the Kemi district in Finland have been identified as a source of Os to the atmosphere (Rodushkin et al. 2007).

Reimann and Niskavaara (2006) estimated that 2.2 metric tons Pd (1.1 % of global annual production) and 0.8 metric tons Pt (0.5 % of global annual production) were emitted annually by the Monchegorsk smelter in the mid 1990s. Based on these estimates, global smelter emissions could exceed 5 % of the annual Pt and Pd productions, equivalent to 9 metric tons Pt and 10 metric tons Pd. In contrast, Pt and Pd emissions estimated using Cu emissions rates from Cu-Ni production (Pacyna 1984) amount to only 0.3–0.7 metric tons per year.

4.3 Industrial PGE Emissions

An increase in Os accumulation rates in a peat record in NW Spain has been observed at the onset of the industrial revolution, indicating that industrial activities are associated with PGE emissions (Rauch et al. 2010). Helmers and Kummerer (1999) note that although industrial emissions are likely, they are difficult to quantify because few data are available for industrial PGE emissions. Elevated PGE concentrations at a site with relatively low traffic in an industrial area in Mexico City were attributed to industrial PGE emissions (Rauch et al. 2006). Sewage from a microelectronics factory in Germany contained 11–33 ng Pt L^{-1} (Laschka and Nachtwey 2000). High PGE concentrations were found in soil near a PGE processing plant in Germany (Zereini et al. 1998). Comparison of PGE distribution patterns near the plant and aside roads shows that industrial and automobile PGE emissions are characterized by different relative PGE abundances. PGE abundance ratios could therefore be used to differentiate between these sources. However, the abundance ratios for industrial sources depend on the type of industrial activity and would need to be determined.

4.4 PGE Emissions from Medical Treatment Centers

Platinum-based drugs, including cisplatin (cis-diammine-dichloro-platinum[II]) and carboplatin (diamine[1,1-cyclobutanedicarboxylato] platinum[II]), are used in the treatment of several forms of cancer. Platinum is excreted by the patients after treatment with Pt-based drugs and is found in hospital effluents at concentrations ranging from <10 ng L^{-1} to 3.5 μg L^{-1}. Pt is subsequently diluted in the municipal wastewater system to concentrations 10 ng L^{-1} in sewage effluents (Kummerer et al. 1999; Lashka and Nachtwey 2000). Emissions are expected to be in form of soluble compounds, including administered drugs and their derivatives (Kummerer et al. 1999). In addition, patients that have undergone treatment with Pt drugs are expected to excrete Pt for a period of over 8 years, indicating that Pt is also released outside of medical facilities (Schierl et al. 1995). Evidence based on the unique isotope signature of industrial Os led Esser and Turekia (1993) to argue that this element is released from biomedical facilities where it is used as a stain fixative in electron microscopy applications.

4.5 PGE in Urban Sewage and Waste

Elevated PGE concentrations have been reported in sewage and waste (Esser and Turekian 1993; Lashka and Nachtwey 2000; Jackson et al. 2010). Sewage and waste potentially become secondary PGE sources, leading to PGE emissions during treatment, reuse or disposal. Depending on characteristics of the sewage network, sewage discharges can result in the release of PGE into the aquatic environment. Wastewater treatment plants in Munich, Germany released 1.3 kg Pt yr^{-1} into local rivers (Lashka and Nachtwey 2000). The use of sewage sludge in agriculture has been identified as a source of PGE in soils (Helmers and Kummerer 1999). PGE enrichments have also been found in incinerator ash, reflecting the occurrence of PGE in municipal waste (Jackson et al. 2010). Elevated Os concentrations in coastal marine sediments have been attributed to sewage discharges into Massachusetts and Cape Cod bays, USA, based on the good correlation of Os concentrations with Ag concentrations and co-variations in Os isotopic composition that point to an anthropogenic source of the Os (Ravizza and Bothner 1996). However, a later study performed in Boston Harbor, USA, reported a large discrepancy between Pt and Pd fluxes estimated from sediment concentrations and fluxes associated with sludge and effluent release, suggesting that sewage discharges are not the main source of these elements to Massachusetts Bay (Tuit et al. 2000).

5 Occurrence of PGE in Remote Environments and Implication for PGE Sources

Elevated PGE concentrations in remote environments have provided evidence for a widespread environmental contamination by anthropogenic activities, as well as information on the contribution of PGE sources to the global biogeochemical cycle of PGE (Barbante et al. 2001, 2004; Moldovan et al. 2007; Rauch et al. 2010; Sen et al. 2013).

5.1 Atmospheric PGE Dispersion

The extent of PGE dispersion from various sources is uncertain. Automobile emissions are expected to have a relatively limited dispersion because PGE are bound to fine particulates. A sharp decrease in PGE concentrations has been observed within a few meters from automobile traffic (Jarvis et al. 2001; Ely et al. 2001; Helmers 1996). However, PGE concentrations remain elevated 100 m away from roads (Jarvis et al. 2001; Ely et al. 2001; Helmers 1996). Industrial emissions from a PGE processing plant in Germany could be tracked for longer distances than automobile catalyst emissions, possibly due to smaller particle sizes and emissions through smoke stacks at greater height (Zereini et al. 1998). Regional dispersion of PGE from mining and ore processing plants has been demonstrated in both South Africa (Rauch and Fatoki 2010) and Russia (Reimann and Niskavaara 2006). Background concentrations were reached within 200 km of Russian smelters (Reimann and Niskavaara 2006). However, the emission of fine PGE-containing particles support the notion of more widespread dispersion (Rauch et al. 2005b), and it has been suggested that both metal production activities and automobile catalysts contribute to the global PGE cycle through long-range atmospheric transport (Barbante et al. 2001; Moldovan et al. 2007; Rauch et al. 2005b).

5.2 Sources of PGE in Rural Aerosols

PGE concentrations and Os isotopic composition (^{187}Os/^{188}Os) in airborne particles in Woods Hole, USA, reveal complex anthropogenic sources (Sen et al. 2013). Woods Hole is located more than 100 km away from the nearest urban center and more than 30 km from any industrial complex. PGE concentrations in Woods Hole aerosols are an order of magnitude below urban concentrations and vary by an order of magnitude. The ^{187}Os/^{188}Os range from 0.132 to 1.074, indicating contributions from different sources. Erosion of the earth's continental crust for instance is characterized by a radiogenic Os signature with an average ^{187}Os/^{188}Os of 1.4 (Peucker-Ehrenbrink and Jahn 2001). In contrast, commercial Os has an unradiogenic isotopic composition because it is mined from ore deposits that are genetically linked to sources in the Earth's mantle, a reservoir with 2–3 orders of magnitude higher PGE concentrations than the continental curst. The Earth's mantle is characterized by a low ^{187}Os/^{188}Os of $\sim$0.1–0.2 (Meisel et al. 1996) that reflects the small time-integrated ratio of the partent isotope (^{187}Re), a moderately incompatible element during mantle melting, to Os. For this reason automobile catalysts are characterised by unradiogenic Os isotopic compositions (Poirier and Gariepy 2005). Pt/Rh and ^{187}Os/^{188}Os indicate that ore smelting is the primary PGE source in airborne particles in Woods Hole, with possible minor contributions from automobile catalyst emissions and fossil fuel combustion (Sen et al. 2013).

5.3 Sources of Os in a Peat Record of Atmospheric Deposition

Evidence for unidentified Os sources has been obtained from a ca. 7000-year long peat record of atmospheric Os accumulation and isotopic composition from an ombrotrophic peat bog in NW Spain (Fig. 3a) (Rauch et al. 2010).

The Os record shows that human influence on Os accumulation in the environment started with early metal mining (ca. 4,700–2,500 years before present [BP]), possibly linked to mining and smelting of copper ores. Osmium accumulation remained elevated thereafter with a maximum during the Roman occupation of the Iberian Peninsula. A further increase is observed starting with the industrial revolution in ca. 1750 AD. While the Os isotopic composition is consistent with a two-component mixing between a radiogenic Os source (erosion) and an unradiogenic Os source (metal mining) until the industrial revolution, a shift in isotopic composition in the more recent samples indicates that at least three components contribute to Os accumulation (Fig. 3b). A source with high Os concentration and unradiogenic Os isotopic composition points to metal production and catalysts, a source with low Os concentration and radiogenic Os isotopic composition is consistent with input from erosion, and a source with high Os concentration and radiogenic Os isotopic composition has been linked to fossil fuel combustion (Rauch et al. 2010).

The Os record at PVO indicates that fossil combustion is a source of PGE to the environment. Platinum concentrations in gasoline are on the order of 1–6 ng L^{-1}, corresponding to an emission of 0.1–0.6 ng km^{-1} for a gasoline consumption of 10 L per 100 km (Hoppstock and Michulitz 1997). Pt emissions from gasoline use are estimated at 1–8 kg yr^{-1}. Platinum concentrations in coal have been estimated at 0.1–1 ng g^{-1} (Oman et al. 1997), implying an emission of 0.001–0.2 metric tons yr^{-1} if emission rates are 0.1–2 %. These estimates are suggestive of fossil fuel combustion contributing to the global as well as urban PGE fluxes and cycles.

5.4 Source of PGE in Snow and Ice

Elevated PGE concentrations have been reported in European mountain regions and in Central Greenland. PGE sources at these sites have been identified using PGE ratios, atmospheric trajectory modelling and comparison of PGE concentration trends with metal use or anthropogenic activities. For instance, Pt, Pd, and Rh have been measured in fresh snow samples in the French Pyrenees Mountains. Atmospheric trajectory models indicate that elevated PGE concentrations are associated with both automobile catalyst emissions and Russian PGE production (Moldovan et al. 2007). The main advantages of these records are excellent chronologic information and the very low natural PGE background in ice and snow. However, these records must be interpreted with care, as the low natural background makes these matrices susceptible to contamination during and after sampling.

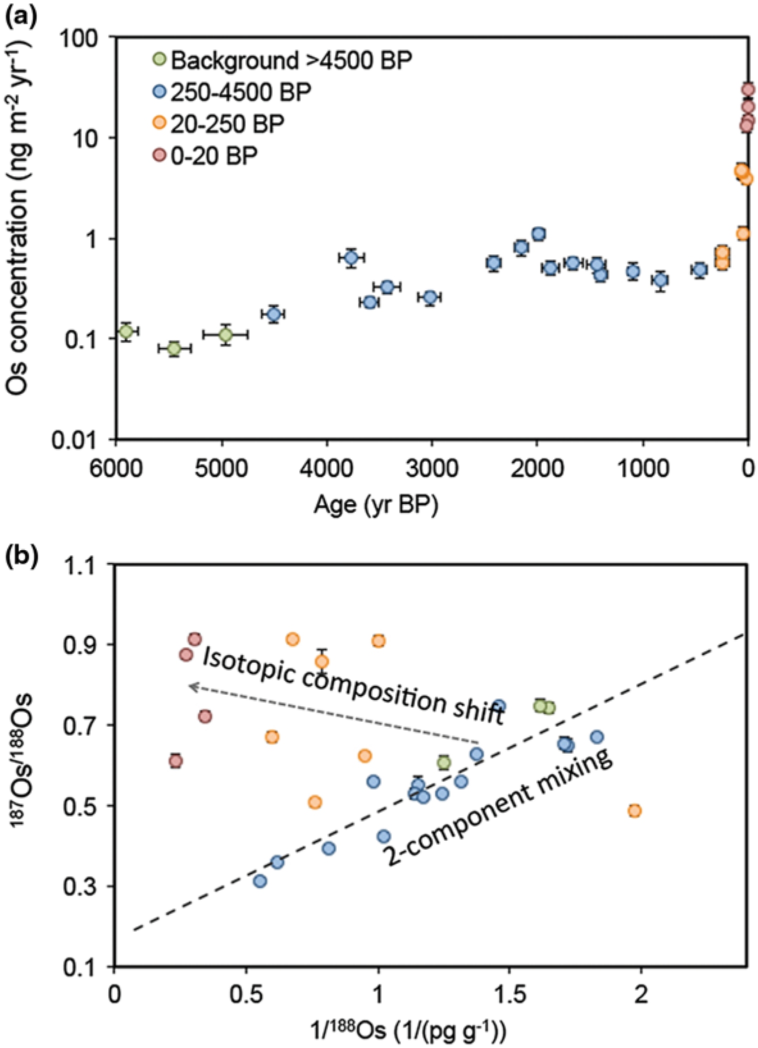

Fig. 3 **a** Changes in Os accumulation in Northwest Spain; **b** Plot of ^{187}Os/^{188}Os versus 1/^{188}Os showing a shift in isotopic composition at the Penido de Vello bog. The pre-industrial period (>250 BP) is characterized by a two-component mixing between an Os-poor radiogenic (high ^{187}Os/^{188}Os) source and an Os-rich unradiogenic (low ^{187}Os/^{188}Os) source. The ^{187}Os/^{188}Os deviate from the two-component mixing line after the onset of the industrial revolution. *Error bars* represent 2 standard deviations (Rauch et al. 2010)

Elevated PGE concentrations have been reported in ice at Summit in Central Greenland, with a sharp concentration increase after 1990 (Barbante et al. 2001). PGE abundance ratios in Greenland ice and atmospheric trajectory models make contributions from multiple sources such as automobile traffic and Russian smelters, likely (Rauch et al. 2005b). The late increase in PGE concentrations in Greenland

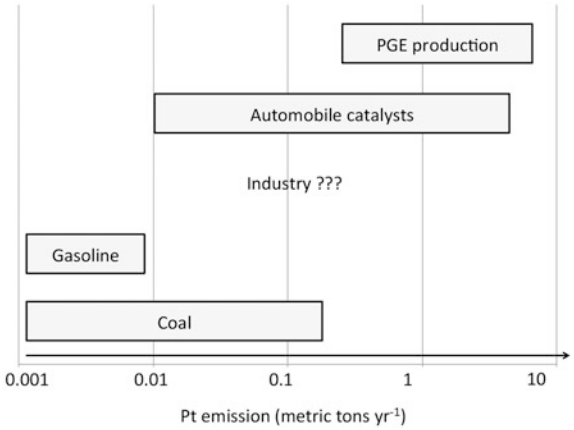

Fig. 4 Estimates of annual global emissions from identified anthropogenic PGE sources into the atmosphere. No estimates are provided for industrial emissions owing to unavailability of emission rates

compared to the introduction of catalysts in the USA in 1975 may point to the predominance of Europe as a source area, as catalysts were introduces in Europe about a decade later. Curiously, there is no direct relationship between the concentration trend in Greenland and either Russian production or the PGE demand for catalysts. It is therefore likely that elevated PGE concentrations in central Greenland are the result of long-range transport from both urban areas where automobile exhaust catalysts are in use and Russian smelters. It would be worthwhile to scrutinize these ice records for the temporal evolution of other tracers of anthropogenic contamination. Such records may point to yet undiscovered sources of PGE to the environment.

6 Conclusion

Available information on the emission and environmental occurrence of PGE indicates that automobile catalysts may not be the single most important PGE source, but that anthropogenic PGE emissions stem from a range of anthropogenic activities. In urban areas, potential sources include automobile catalysts, industrial processing, fossil fuel combustion and medical centers. The dispersion of PGE from urban sources and emissions from PGE production facilities contribute to the global biogeochemical cycles of PGE. A comparison of atmospheric PGE emissions from a variety of potential sources indicates that PGE production activities, automobile catalysts and coal combustion are potentially equally important sources of PGE (Fig. 4). There are, however, significant uncertainties in emission estimates owing to significant variations in reported emission estimates. For instance, while available data are consistent with the release of PGE from industrial activities, it is not yet possible to quantify industrial PGE emissions. A further complication lies in our limited understanding of PGE dispersion that makes it very challenging to determine the geographical extent of PGE contamination from these sources.

Further research should focus on two parallel approaches; firstly, emission rates from identified PGE sources should be better quantified and dispersion mechanisms assessed in an attempt to determine the extent of PGE contamination from each source. Secondly, detailed environmental records should be obtained and source identification methods refined in order to assess the contribution from different PGE sources, and to detect any yet unidentified sources of PGE to the environment.

References

Barbante C, Veysseyre A, Ferrari C, Van de Velde K, Morel C, Capodaglio G, Cescon P, Scarponi G, Boutron C (2001) Greenland snow evidence of large scale atmospheric contamination for platinum, palladium, and rhodium. Environ Sci Technol 35:835–839

Barbante C, Schwikowski M, Doring T, Gaggeler HW, Schotterer U, Tobler L, Van De Velde K, Ferrari C, Cozzi G, Turetta A, Rosman K, Bolshov M, Capodaglio G, Cescon P, Boutron C (2004) Historical record of European emissions of heavy metals to the atmosphere since the 1650 s from Alpine snow/ice cores drilled near Monte Rosa. Environ Sci Technol 38:4085–4090

Ely JC, Neal CR, Kulpa CF, Schneegurt MA, Seidler JA, Jain JC (2001) Implications of platinum-group element accumulation along US roads from catalytic-converter attrition. Environ Sci Technol 35:3816–3822

Esser BK, Turekian KK (1993) Anthropogenic osmium in coastal deposits. Environ Sci Technol 27:2719–2724

Fritsche J, Meisel T (2004) Determination of anthropogenic input of Ru, Rh, Pd, Re, Os, Ir and Pt in soils along Austrian motorways by isotope dilution ICP-MS. Sci Total Environ 325:145–154

Goldschmidt VM (1922) Der Stoffwechsel der Erde. Videnskapsselskapets Skrifter. I. Mat. -Naturv. Klasse 11:3–25

Gomez B, Palacios MA, Gomez M, Morrison GM, Rauch S, McLeod C, Ma R, Caroli S, Alimonti A, Schramel P, Zischka M, Pettersson C, Wass U (2002) Platinum, palladium and rhodium contamination in airborne particulate matter and road dust of European cities. Risk assessment evaluation. Sci Total Environ 299:1–19

Helmers E (1996) Elements accompanying platinum emitted from automobile exhaust catalysts. Chemosphere 33:405–419

Helmers E (1997) Platinum emission rate of automobiles with catalytic converters - Comparison and assessment of results from various approaches. Environ Sci Pollut Res 4:100–103

Helmers E, Kummerer K (1999) Anthropogenic platinum fluxes: Quantification of sources and sinks, and outlook. Environ Sci Pollut Res 6:150–150

Hoppstock K, Michulitz M (1997) Voltammetric determination of trace platinum in gasoline after Wickbold combustion. Anal Chim Acta 350:135–140

Jackson MT, Sampson J, Prichard HM (2010) Platinum-group elements in sewage sludge and incinerator as in the United Kingdom: Assessment of PGE sources and mobility in cities. Sci Total Environ 408:1276–1285

Jarvis KE, Parry SJ, Piper JM (2001) Temporal and spatial studies of autocatalyst-derived platinum, rhodium, and palladium and selected vehicle-derived trace elements in the environment. Environ Sci Technol 35:1031–1036

Klee RJ, Greadel TE (2004) Elemental cycles: A status report on human or natural dominance. Annu Rev Environ Resour 29:69–107

Konig HP, Hertel RF, Koch W, Rosner G (1992) Determination of Platinum Emissions from a 3-Way Catalyst-Equipped Gasoline-Engine. Atmos Environ A-Gen 26:741–745

Kummerer K, Helmers E, Hubner P, Mascart G, Milandri M, Reinthaler F, Zwakenberg M (1999) European hospitals as a source for platinum in the environment in comparison with other sources. Sci Total Environ 225:155–165

Lashka D, Striebel T, Daub J, Nachtwey M (1996) Platin im Regenfluß einer Straße. Umweltwissenschaften Schadstoff-Forschung 8:124–129

Lashka D, Nachtwey M (2000) Traffic-borne platinum pollution in municipal sewage treatment plants. In: Alt F, Zereini F (eds) Anthropogenic platinum group elements and their impact on man and the environment. Springer-Verlag, Berlin, pp 25–32

Matthey J (2013) Market data tables http://www.platinum.matthey.com/publications/market-data-tables. Accessed 28 Nov 2013

Meisel T, Walker RJ, Morgan JW (1996) The osmium isotopic composition of the Earth's primitive upper mantle. Nature 383:517–520

Moldovan M, Palacios MA, Gomez MM, Morrison G, Rauch S, McLeod C, Ma R, Caroli S, Alimonti A, Petrucci F, Bocca B, Schramel P, Zischka M, Pettersson C, Wass U, Luna M, Saenz JC, Santamaria J (2002) Environmental risk of particulate and soluble platinum group elements released from gasoline and diesel engine catalytic converters. Sci Total Environ 296:199–208

Moldovan M, Rauch S, Morrison GM, Gomez M, Palacios MA (2003) Impact of ageing on the distribution of platinum group elements and catalyst poisoning elements in automobile catalysts. Surf Interface Anal 35:354–359

Moldovan M, Veschambre S, Amouroux D, Bénech B, Donard OFX (2007) Platinum, palladium, and rhodium in fresh snow from the Aspe Valley (Pyrenees Mountains, France). Environ Sci Technol 41:66–73

Niskavaara H, Kontas E, Reimann C (2004) Regional distribution and sources of Au, Pd and Pt in moss and O-, B- and C-horizon podzol samples in the European Arctic. Geochemistry-Exploration Environment Analysis 4:143–159

Noddack I, Noddack W (1931) Die Häufigkeit der Platinmetalle in der Erdrinde. Z phys Chem, Bodenstein-Festband, pp 890–894

Oman CL, Finkelman RB, Tewalt SJ (1997) Concentration of platinum group elements in 122 U. S. Coal samples. USGS Open-File Report 97-53

Pacyna JM (1984) Estimation of the atmospheric emissions of trace elements from anthropogenic sources in Europé. Atmos Environ 18:41–50

Palacios MA, Gomez MM, Moldovan M, Morrison G, Rauch S, McLeod C, Ma R, Laserna J, Lucena P, Caroli S, Alimonti A, Petrucci F, Bocca B, Schramel P, Lustig S, Zischka M, Wass U, Stenbom B, Luna M, Saenz JC, Santamaria J (2000) Platinum-group elements: quantification in collected exhaust fumes and studies of catalyst surfaces. Sci Total Environ 257:1–15

Peucker-Ehrenbrink B, Jahn BM (2001) Rhenium-osmium isotope systematics and platinum group element concentrations: Loess and the upper continental crust. Geochemistry Geophysics Geosystems 2: 1061. doi:10.109/2001GC000172

Poirier A, Gariepy C (2005) Isotopic signature and impact of car catalysts on the anthropogenic osmium budget. Environ Sci Technol 39:4431–4434

Qi L, Zhou MF, Zhao Z, Hu J, Huang Y (2011) The characteristics of automobile catalyst-derived platinum group elements in road dusts and roadside soils: a case study in the Pearl River Delta region, South China. Environ Earth Sci 64:1683–1692

Rauch S, Morrison GM, Motelica-Heino M, Donard OFX, Muris M (2000) Elemental associations and fingerprinting of traffic related metals in road sediments. Environ Sci Technol 34:3119–3123

Rauch S, Hemond HF, Peucker-Ehrenbrink B (2004) Recent changes in platinum group element concentrations and osmium isotopic composition in sediments from an urban lake. Environ Sci Technol 38:396–402

Rauch S, Hemond HF, Peucker-Ehrenbrink B, Ek K, Morrison GM (2005a) Platinum group element concentrations and osmium isotopic composition in airborne particles from Boston, Massachusetts. Environ Sci Technol 39:9464–9470

Rauch S, Hemond HF, Barbante C, Owari M, Morrison GM, Peucker-Ehrenbrink B, Wass U (2005b) Importance of automobile exhaust catalyst emissions for the deposition of platinum, palladium, and rhodium in the Northern Hemisphere. Environ Sci Technol 39:8156–8162

Rauch S, Peucker-Ehrenbrink B, Molina LT, Molina MJ, Ramos R, Hemond HF (2006) Platinum group elements in airborne particles in Mexico city. Environ Sci Technol 40:7554–7560

Rauch S, Kylander ME, Weiss DJ, Martinez-Cortizas A, Heslop D, Olid C, Mighall TM, Hemond HF (2010) Anthropogenic forcings on the surficial osmium cycle. Environ Sci Technol 44:881–887

Rauch S, Fatoki OS (2010) Platinum and lead in South African road dust. In: Rauch et al. (eds) Highway and urban environment. Springer, The Netherlands, pp 161–166. ISBN 978-90-481-3043-6

Rauch S, Fatoki OS (2013) Anthropogenic platinum enrichment in the vicinity of mines in the bushveld igneous complex. South Africa. Water Air Soil Pollution 224:1395. doi:10.1007/s11270-012-1395-y

Ravizza GE, Bothner MH (1996) Osmium isotopes and silver as tracers of anthropogenic metals in sediments from Massachusetts and Cape Cod bays. Geochim Cosmochim Acta 60:2753–2763

Reimann C, Niskavaara H (2006) Regional distribution of Pd, Pt and Au-emissions from the nickel industry on the Kola peninsula, NW-Russia, as seen in Moss and Hummus samples. In: Zereini F, Alt F (eds) Palladium emissions into the environment. Springer, Heidelberg, Germany, pp 53–70

Rodushkin I, Engström E, Sörlin D, Pontér C, Baxter DC (2007) Osmium in environmental samples from Northeast Sweden. Part II. Identification of anthropogenic sources. Sci Total Environ 386:159–168

Schierl R, Rohrer B, Hohnloser J, Hohnloser H (1995) Long-term excretion in patients treated with cisplatin. Cancer Chemother Pharmacol 36:75–78

Sen IS, Peucker-Ehrenbrink B (2012) Anthropogenic disturbance of element cycles at the earth’s surface. Environ Sci Technol 46:8601–8609

Sen IS, Peucker-Ehrenbrink B, Geboy N (2013) Complex anthropogenic sources of platinum group elements in aerosols on Cape Cod, USA. Environ Sci Technol 47:10188–10196

Tuit CB, Ravizza GE, Bothner MH (2000) Anthropogenic platinum and palladium in the sediments of Boston harbor. Environ Sci Technol 34:927–932

Wedepohl KH (1995) The composition of the continental-crust. Geochim Cosmochim Acta 59:1217–1232

Zereini F, Dirksen F, Skerstupp B, Urban H (1998) Sources of anthropogenic platinum-group elements (PGE): Automotive catalysts versus PGE-processing industries. Environ Sci Pollut Res 5:223–230

Zereini F, Skerstupp B, Rankenburg K, Dirksen F, Beyer JM, Claus T, Urban H (2000) Anthropogenic emission of platinum- group elements (Pt, Pd and Rh) into the environment: con- centration, distribution and geochemical behaviour in soils. In: Alt F, Zereini F (eds) Anthropogenic platinum group elements and their impact on man and the environment. Springer, Berlin, pp 73–83

Zereini F, Alt F, Messerschmidt J, Von Bohlen A, Liebl K, Puttmann W (2004) Concentration and distribution of platinum group elements (Pt, Pd, Rh) in airborne particulate matter in Frankfurt am Main, Germany. Environ Sci Technol 38:1686–1692

Impact of Platinum Group Element Emissions from Mining and Production Activities

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Abstract South Africa and Russia are the world's leading platinum group elements (PGE) producers with over 80 % of the global PGE output. Studies performed in the Bushveld Igneous Complex in South Africa and on the Kola Peninsula in Russia show that PGE mining and production activities are important regional PGE sources. Elevated PGE concentrations have been found in snow, soil, road dust, grass, moss and humus collected near PGE mining and production sites. The occurrence of elevated PGE concentrations near mining sites raises concern over environmental effects and exposure of the local population. Studies on the occurrence of PGE in remote environments also suggest that emissions from PGE production activities contribute to the global biogeochemical cycle of the PGE. The loss of PGE during metal production could be as much as 5 % of the global supply and represents a substantial economic loss. Studies on the impact of PGE mining and production activities are few. Further research is needed to better assess the environmental impact of PGE emissions from mining and production activities.

1 Introduction

Studies on the environmental relevance of the platinum group elements (PGE) have until now largely focused on urban and roadside environments where elevated PGE concentrations have been reported as a result of automobile catalyst emissions (Ravindra et al. 2004; Rauch and Morrison 2008). Although metal production

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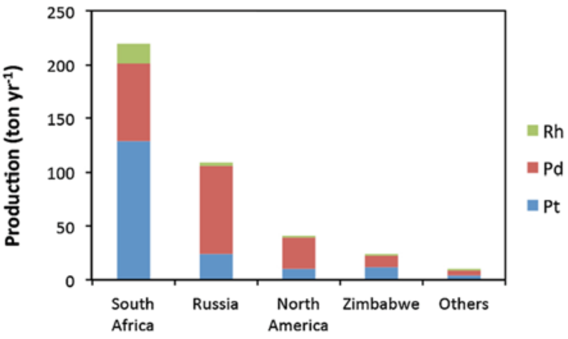

Fig. 1 PGE production estimates by country for 2013 (Data Johnson-Matthey 2013)

activities are recognised to be an important source of metals into the environment (Nriagu and Pacyna 1988; Dudka and Adriano 1997), PGE emission from mining and production activities have only received little attention. Recent studies performed in remote environments indicate however that additional PGE sources contribute to the global biogeochemical cycles of these element and metal production activities have been suggested as a potential source of PGE into the environment (Barbante et al. 2001; Rauch et al. 2005; Moldovan et al. 2007; Rauch et al. 2010; Sen et al. 2013).

PGE are present at trace concentrations in the Earth's upper continental crust (Peucker-Ehrenbrink and Jahn 2001) and economic recovery is only possible at a few sites where PGE concentrations are sufficiently high. PGE are mined from primary deposits where they are typically in igneous minerals and associate to other elements (e.g. Cu and Ni) in igneous rocks, and secondary deposits formed by erosion and relocation of PGE in pure metallic form. Primary deposits, such as the Bushveld Igneous Complex (BIC) in South Africa and the Norilsk/Talnakh complex in Russia, account for most of the PGE production. It is estimated that 179 tons Pt, 197 tons Pd and 22 tons Rh were produced in 2013, and South Africa and Russia accounted for 82 % of the global PGE production (Fig. 1). The remaining 18 % were mainly produced by Canada, the USA and Zimbabwe (Johnson-Matthey 2013).

This chapter summarizes current knowledge on PGE emissions from PGE mining and production activities in South Africa and Russia, as well as their contribution to the global biogeochemical cycles of the PGE.

2 Impact of PGE Mining in South Africa

2.1 *Mining Areas*

South Africa is the world's largest PGE producer with 72 % of Pt production, 37 % of Pd production and 80 % of Rh production in 2013 (Johnson-Matthey 2013). South Africa's PGE resources are located in the Bushveld Igneous Complex (BIC) in the Northern part of the country (Fig. 2). The BIC is the world's largest mafic-ultramafic

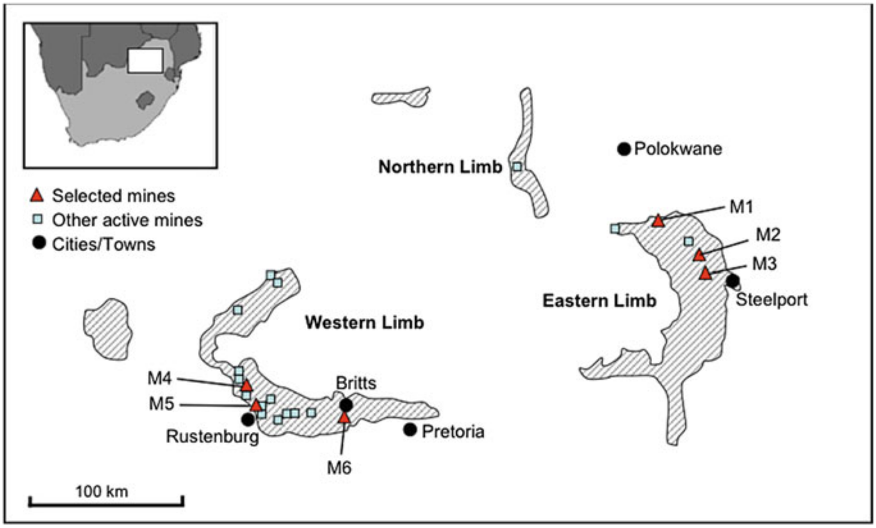

Fig. 2 Map of the Bushveld Igneous Complex with the location of mines (M1–M6) in the Rauch and Fatoki (2013) study

intrusion with an area of 65,000 km^2 and 75 % of the world's Pt resources (Cawthorn 1999). Mining has until recently concentrated on the shallower Merinsky Reef in the western limb of the BIC because of higher grade, lower chromite content and easier access to mining sites. Increasing demand and decreasing reserves are now resulting in the exploitation of the deeper Upper Group 2 (UG2) chromitite layer and of the eastern limb of the BIC. In 2006 mining of UG2 was expected to represent as much as 60 % of the total ore processed in the BIC and 18 % of the production was expected to take place in the eastern limb (Johnson-Matthey 2003). Processing plants and smelters are operated in both the Western and Eastern Limbs of the BIC.

2.2 *Platinum Concentrations in the Vicinity of PGE Mines in the BIC*

Elevated Pt and Pd concentrations in the BIC were first reported in the context of geochemical mapping. Concentrations exceeding 180 ng Pt g^{-1} and 99 ng Pd g^{-1} were found in soil in the BIC and mining operations were suggested as a possible Pt and Pd source (Wilhelm et al. 1997). Potential PGE emissions by mining activities in the BIC were however not investigated further.

Elevated Pt concentrations have been reported near selected mines (M1–M6 in Fig. 2) in the BIC (Rauch and Fatoki 2013). Platinum concentrations in topsoil ranged from 9.9 ± 0.7 ng g^{-1} near an underground shaft to 653 ± 40 ng g^{-1} near a PGE smelter (Fig. 2). In comparison, Pt concentrations in the BIC were 4–250

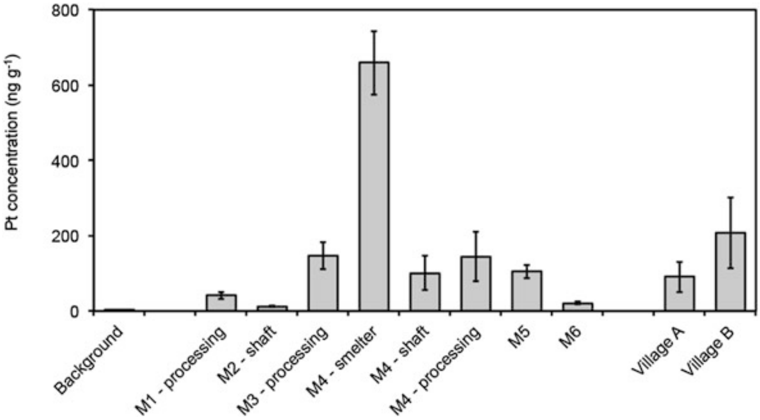

Fig. 3 Pt concentrations in top soil collected at a background site, near PGE mines (M1–M6) and in villages located near mine M4 (Data Rauch and Fatoki 2013)

times larger than Pt concentrations at a background site. The observed variation in Pt concentrations is attributed to the type of activity in the direct vicinity of the sampling point and indicate that smelters are more important Pt sources than mining from underground shafts or ore processing (Fig. 3).

Pt was found to be enriched in fine particles (<125 μm) near the smelter, whereas a more even particle size distribution was found at the processing plant (Rauch and Fatoki 2013). Ore processing essentially consists of milling and separation by flotation, and may therefore only result in the emission coarse particles. In contrast, smelting involves high temperature processes that may result in the formation of finer particles.

Elevated Pt concentrations were also found in grass collected at mine M4 and in nearby towns with the highest concentration (256 ± 122 ng g^{-1}) measured near the smelter at mine M4. Exposure experiments in the lab showed that uptake from contaminated soil is relatively limited and the occurrence of PGE in grass is therefore attributed to deposition of Pt-containing aerosols.

2.3 *Platinum Concentrations in South African Road Dust*

Road dust was collected in four South African cities to assess the relative importance of automobile catalysts and PGE production activities (Rauch and Fatoki 2010). Average Pt concentrations in road dust ranged from 4 ng g^{-1} in Cape Town to 223 ng g^{-1} in Rustenburg (Fig. 4) with a minimum concentration of 2 ng g^{-1} along highway N2 in Cape Town and a maximum concentration of 391 ng g^{-1} at Mandela Street in Rustenburg. The results show that automobile catalysts are a minor source of Pt into the South African environment with relatively low

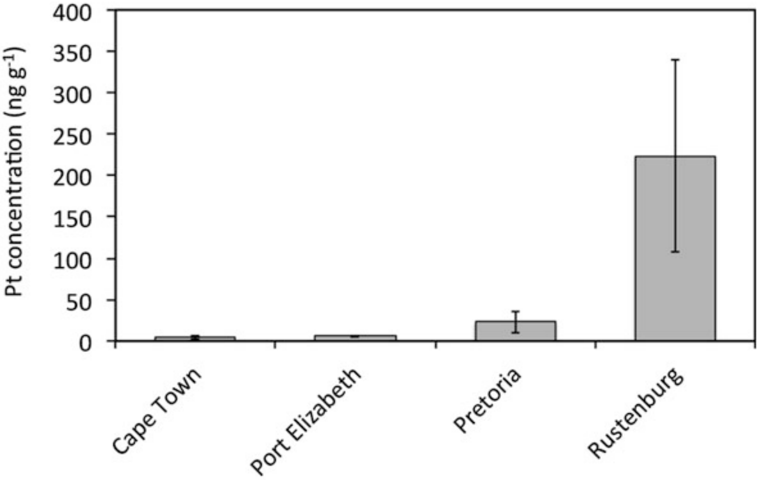

Fig. 4 Average Pt concentration in road dust collected in South African cities (Data Rauch and Fatoki 2010)

concentrations at high traffic sites in Cape Town and Port Elizabeth. Rustenburg is located in the Western Bushveld and elevated Pt concentrations are associated with PGE mining and production activities. Elevated Pt concentrations in Pretoria relative to Cape Town and Port Elizabeth indicate that Pt emitted in the BIC is dispersed at regional scale. Pretoria is located 150 km East of Rustenburg.

3 Impact of PGE Mining in Russia

3.1 Mining Areas

PGE production in Russia dates back to the early nineteenth century when alluvial deposits were discovered in the Ural Region. Today, Russia is the world's second largest PGE producer and the largest Pd producer with 14 % of Pt production, 41 % of Pd production and 12 % of Rh production (Johnson-Matthey 2013). PGE production activities are located at 5 sites across the country (Fig. 5).

The Norilsk/Talnakh site on the Taimyr Peninsula in Northern Siberia accounts for most of Russia's PGE production. PGE at Norilsk/Talnakh occur in large sheets of PGE-containing copper-nickel ores associated with a sequence of igneous intrusions. PGE occur in massive sulphide ores, copper-rich ores and disseminated ores and are produced along with copper and nickel. While the Norilsk/Talnakh deposit is larger than the Bushveld Igneous Complex, PGE grades vary widely. Lower grade nickel-copper ores with PGE by-products are produced on the Kola Peninsula. Concentrating and smelting operations are performed at both the Norilsk/Talnakh and the Kola Peninsula sites (Johnson-Matthey 2004; Reimann and Niskavaara 2006).

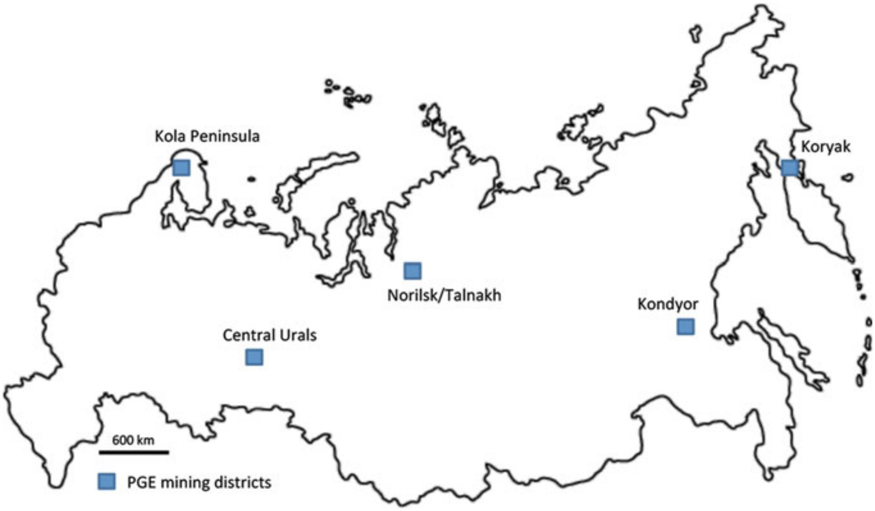

Fig. 5 Map of Russia with PGE mining districts (adapted from Johnson-Matthey 2004)

Platinum is also produced from Koryak and Kondyor, two alluvial deposits in the far Eastern regions of Russia. Alluvial platinum deposits in the Urals are still being mined, but account for a small fraction of Russian PGE production (Johnson-Matthey 2004).

3.2 *Platinum Concentrations in the Vicinity of PGE Mines on the Kola Peninsula*

The Norilsk/Talnakh area and the Kola Peninsula are heavily polluted by metal production industries (Blacksmith Institute 2013; Zhulidov et al. 2011; Reimann et al. 1998). Studies on PGE contamination in Russia have only focused on the Kola Peninsula; there is no published information on the contamination levels at the Norilsk/Talnakh site, despite higher production levels.

Elevated PGE concentrations have been reported in O-horizon soil near the Ni refinery in Monchegorsk, the Ni smelter in Nikel and the Cu–Ni ore roasting plant in Zapolyarnij (Niskavaara et al. 2004; Reimann and Niskavaara 2006). The highest concentrations (218 ng Pt g^{-1}, 656 ng Pd g^{-1}) were found near the Monchegorsk refinery, which processes PGE-rich ores from the Norilsk/Talnakh deposits, whereas local Pechenga ores with lower PGE contents are process in Nickel and Zapolyarnij (Reimann and Niskavaara 2006). Average concentrations of 49.6 ng Pt g^{-1}, 187.6 ng Pd g^{-1} and 1.4 ng Rh g^{-1} have been reported in topsoil near the Monchegorsk plant (Boyd et al. 1997). In comparison, median concentrations of 0.62 ng Pt g^{-1} and 0.45 ng Pd g^{-1} have been reported in O-horizon soil in the European Artic (Finland, Norway, Russia) (Reimann and Niskavaara 2006).

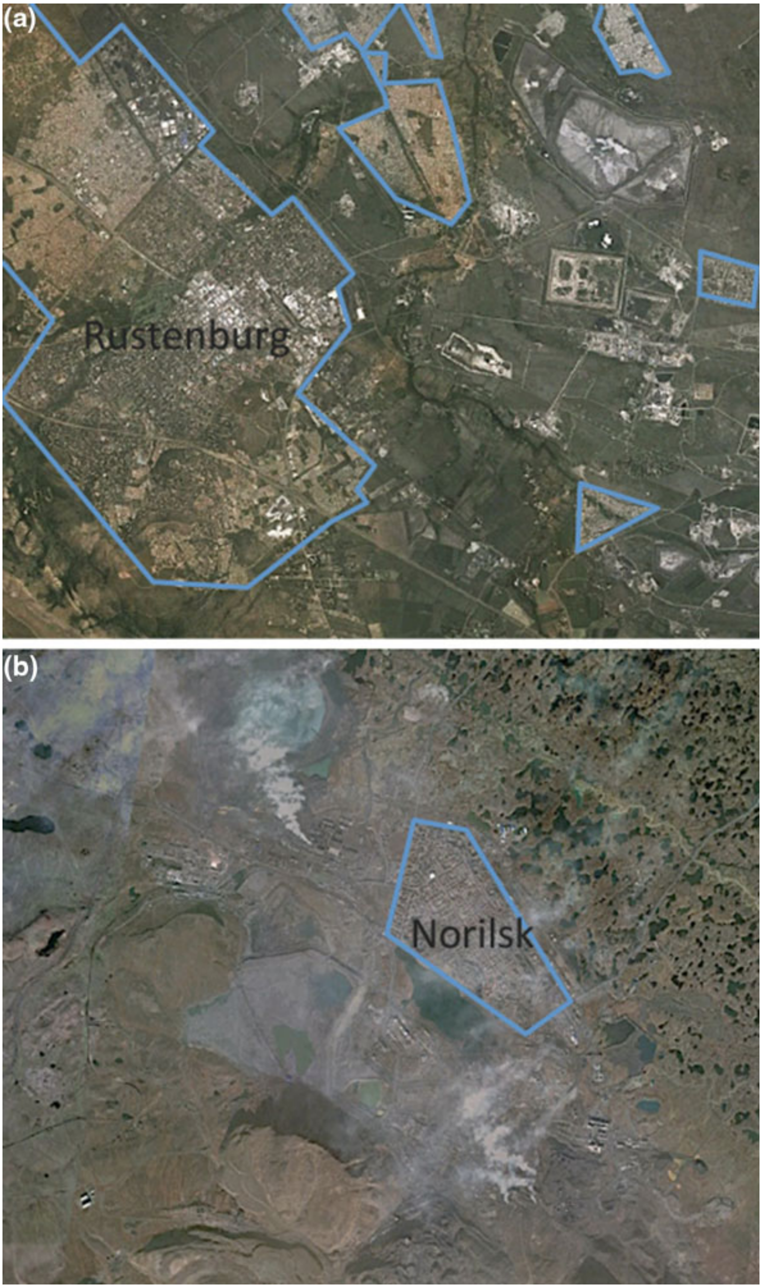

Fig. 6 Satellite images of the Rustenburg (South Africa, **a**) and Norilsk (Russia, **b**) areas showing the proximity of mining operations to human settlements (*marked in blue*). Images reproduced from Google Earth

PGE concentrations in snow were found to be in the range <1–650 ng Pt l^{-1}, <1–2770 ng Pd l^{-1}, <0.5–19 ng Rh l^{-1} near the Monchegorsk, Nikel and Zapolyarnij plants). The highest concentrations were found at the Monchegorsk plant (Gregurek et al. 1999).

The PGE concentration pattern in soil and snow is similar to that of processed ores, suggesting that PGE are emitted in the form of ore dust. The PGE concentration pattern in soil reflects that of Talnakh ores processed at the Monchegorsk plant, whereas concentration pattern in snow suggest that both Norilsk and Pechenga (Kola Peninsula) ores contribute to elevated PGE concentrations on the Kola Peninsula. PGE concentration patterns in soil and snow samples also indicate that there is no preferential leaching or redistribution of emitted PGE (Boyd et al. 1997; Gregurek et al. 1999).

4 Implication of PGE Emissions by Mining and Production Activities

4.1 Environmental Impact and Human Exposure

The occurrence of elevated PGE concentrations has no proven environmental impact, possibly due to limited data on chronic effect. Although the occurrence of PGE in grass (Rauch and Fatoki 2013) and moss (Reimann and Niskavaara 2006) near PGE production sites is likely due to atmospheric deposition, it is known that PGE emitted by automobile catalysts can be bioaccumulated (Moldovan et al. 2001; Ek et al. 2004; Haus et al. 2007). Data on the occurrence of PGE in biota near PGE production sites is lacking. In addition, PGE mining and production activities are important point sources of SO_2 and heavy metals (Blacksmith Institute 2013; Zhulidov et al. 2011; Reimann et al. 1998; Boyd et al. 2009). Severe environmental degradation has been observed around the Russian PGE production sites (Zhulidov et al. 2011) and Norilsk is considered to be one of the most contaminated places on Earth (Blacksmith Institute 2013).

Some of the main PGE mining and production sites are located in the direct vicinity of human settlements. Rustemburg (ca. 550,000 inhabitants in the Local Municipality), Norilsk (ca. 175,000 inhabitants) and Monchegorsk (ca. 45,000 inhabitant) are located within a few km of mines, smelter and refineries (Fig. 6). PGE emissions and occurrence of elevated PGE concentrations in the environment raise concern over exposure of the local population. Elevated Pt concentrations were found in soil and grass in two towns located within a few kilometres from mine M4 in the BIC (Rauch and Fatoki 2013). Platinum concentrations in soil in Town A (1 km North of the smelter) and Town B (3 km SW of the smelter) were 73 ± 61 and 109 ± 48 ng g^{-1} in 2008, respectively. The mining companies are also the main employers in these cities, resulting in a combination of both environmental and occupational exposures for many inhabitants. Potential toxic effects at high concentrations include sensitization, mutagenic effects and increased tumor incidence.

4.2 Global Impact of PGE Emissions from Mining

Increasing PGE concentrations in remote environments have been attributed to anthropogenic PGE emissions (Barbante et al. 2001; Rauch et al. 2005; Moldovan et al. 2007; Rauch et al. 2010; Sen et al. 2013). Atmospheric back trajectories indicate that PGE in Central Greenland and in the French Pyrenees partly originate from mining districts in Russia (Rauch et al. 2005; Moldovan et al. 2007). PGE ratios further suggest that anthropogenic PGE deposition in Greenland is the result of emissions from both automobile catalysts and PGE production activities (Rauch et al. 2005). However, studies at the PGE mining and production sites on the Kola Peninsula show that PGE concentrations decrease with increasing distance from the production sites and the prevailing wind direction (Gregurek et al. 1998, 1999). Background Pt and Pd concentrations are reached within 200 km from smelters (Reimann and Niskavaara 2006). Differences may be explained by a stronger influence of the geogenic background in the samples collected in the Kola Peninsula.

4.3 Economic Loss and Recovery

PGE emission by mining and production activities corresponds to a loss of resources. It is estimated that 2.2 tons Pd (1.1 % of global production) and 0.8 tons Pt (0.5 % of global production) were emitted yearly by the Monchegorsk smelter in the mid 1990s (Reimann and Niskavaara 2006). Emission rates at the Monchegorsk smelter indicate that global emissions could represent over 5 % of Pt and Pd production (>10 tons Pd yr^{-1} and >9 tons Pd yr^{-1}). In contrast, Pt and Pd emissions estimated using Cu emissions rates from Cu-Ni production (Pacyna 1984) amount to 0.3–0.7 metric tons per year. Although these numbers are approximate, the emission rates indicate substantial economic losses. Measured PGE concentrations in soil near the smelters in South Africa and Russia also indicate that it would be possible to recover part of the emitted PGE. More detailed feasibility studies should be made to determine the area from which PGE could be recovered.

5 Conclusion

PGE mining and production industries are important local PGE sources. Elevated PGE concentrations have been reported near mining and production operations in South Africa and Russia, raising concern over exposure of the local population and environmental degradation. While the emission of PGE may represent a substantial economic loss, environmental levels near PGE smelters indicate that it would be possible to recover PGE from contaminated soil. There is also some indication that

PGE emissions from PGE production operations contribute to the global biogeochemical cycle of these elements. Studies on PGE emission from mining and production activities are few; there is for instance no published data for the Norilsk/Talnakh operations. Further studies are needed to determine emission rates and assess environmental contamination at local, regional and scales.

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References

Barbante C, Veysseyre A, Ferrari C, Van de Velde K, Morel C, Capodaglio G, Cescon P, Scarponi G, Boutron C (2001) Greenland snow evidence of large scale atmospheric contamination for platinum, palladium, and rhodium. Environ Sci Technol 35:835–839

Blacksmith Institute (2013) The worlds worst 2013: the top ten toxic threats. blacksmith institute, New York, USA. http://www.worstpolluted.org/. Accessed 20 Dec 2013

Boyd R, Niskavaara H, Kontas E, Chekushin V, Pavlov V, Often M, Reimann C (1997) Anthropogenic noble-metal enrichment of topsoil in the Monchegorsk area, Kola peninsula, northwest Russia. Geochem Explor 58:283–289

Boyd R, Barnes S-J, de Caritat P, Chekushin VA, Melezhik V, Reimann C, Zientek M (2009) Emissions from the copper-nickel industry on the Kola Peninsula and at Noril'sk, Russia. Atmos Environ 43:1474–1480

Cawthorn RG (1999) The platinum and palladium resources of the Bushweld Complex. S Afr J Sci 95:481–489

Dudka S, Adriano DC (1997) Environmental impacts of metal ore mining and processing: a review. J Environ Qual 26:590–602

Ek KH, Morrison GM, Rauch S (2004) Environmental routes for platinum group elements to biological materials—a review. Sci Total Environ 334:21–38

Gregurek D, Melcher F, Niskavaara H, Pavlov VA, Reimann C, Stumpfl EF (1999) Platinum-group elements (Rh, Pt, Pd) and Au distribution in snow samples from the Kola Peninsula, NW Russia. Atmos Environ 33:3281–3290

Gregurek D, Reimann C, Stumpfl EF (1998) Trace elements and precious metals in snow samples from the immediate vicinity of nickel processing plants, Kola Peninsula, northwest Russia. Environ Pollut 102:221–232

Haus DN, Zimmermann S, Wiegand J, Sures B (2007) Occurrence of platinum and additional traffic related heavy metals in sediments and biota. Chemosphere 66:619–629

Johnson-Matthey (2003) The expansion of platinum mining in South Africa. In: platinum 2003. Johnson-Matthey, London, UK. pp 14–17

Johnson-Matthey (2004) PGM mining in Russia. In: Platinum 2004. Johnson-Matthey, London, UK. pp 16–21

Johnson-Matthey (2013) Platinum 2013. Johnson-Matthey, London, UK

Moldovan M, Rauch S, Gómez M, Palacios MA, Morrison GM (2001) Bioaccumulation of palladium, platinum and rhodium from urban particulates and sediments by the freshwater isopod *Asellus aquaticus*. Water Res 35:4175–4183

Moldovan M, Veschambre S, Amouroux D, Benech B, Donard OFX (2007) Platinum, palladium, and rhodium in fresh snow from the aspe valley (Pyrenees Mountains, France). Environ Sci Technol 41:66–73

Niskavaara H, Kontas E, Reimann C (2004) Regional distribution and sources of Au, Pd and Pt in moss and O-, B- and C-horizon podzol samples in the European arctic. Geochem Explor Environ Anal 4:143–159

Nriagu JO, Pacyna JM (1988) Quantitative assessment of worldwide contamination of air, water and soils by trace metals. Nature 333:134–139

Pacyna JM (1984) Estimation of the atmospheric emissions of trace elements from anthropogenic sources in Europé. Atmos Environ 18:41–50

Peucker-Ehrenbrink B, Jahn BM (2001) Rhenium-osmium isotope systematics and platinum group element concentrations: loess and the upper continental crust. Geochem Geophys Geosyst 2, 1061

Rauch S, Hemond HF, Barbante C, Owari M, Morrison GM, Peucker-Ehrenbrink B, Wass U (2005) Importance of automobile exhaust catalyst emissions for the deposition of platinum, palladium, and rhodium in the Northern Hemisphere. Environ Sci Technol 39:8156–8162

Rauch S, Morrison GM (2008) The environmental relevance of platinum group elements. Elements 4:259–263

Rauch S, Fatoki OS (2010) Platinum and lead in South African road dust. In: Rauch et al. (Eds) Highway and Urban Environment. Springer, The Netherlands. ISBN 978-90-481-3043-6

Rauch S, Fatoki OS (2013) Anthropogenic platinum enrichment in the vicinity of mines in the bushveld igneous complex. S Afr Water Air Soil Pollut 224:1395

Rauch S, Peucker-Ehrenbrink B, Kylander ME, Weiss DJ, Martinez-Cortizas A, Heslop D, Olid C, Mighall TM, Hemond HF (2010) Anthropogenic forcings on the surficial osmium cycle. Environ Sci Technol 44:881–887

Ravindra K, Bencs L, Van Grieken R (2004) Platinum group elements in the environment and their health risk. Sci Total Environ 318:1–43

Reimann C, Äyräs M, Chekushin VA, Bogatyrev I, Boyd R, de Caritat P, Dutter R, Finne TE, Halleraker JH, Jäger Ø, Lehto O, Niskavaara H, Räisänen ML, Starnd T, Volden T (1998) Environmental Geochemical Atlas of the Central Barents Region. NGU-GTK-CKE Special Publication, Geological Survey of Norway, Trondheim, Norway

Reimann C, Niskavaara H (2006) Regional distribution of Pd, Pt and Au-emissions from the Nickel Industry on the Kola Peninsula, NW-Russia, as seen in moss and hummus samples. In: Zereini F, Alt F (Eds) Palladium emissions into the environment. Springer, Heidelberg, ISBN 978-3-540-29219-7

Sen IS, Peucker-Ehrenbrink B, Geboy N (2013) Complex anthropogenic sources of platinum group elements in aerosols on Cape Cod, USA. Environ Sci Technol 47:10188–10196

Wilhelm HJ, Zhang H, Chen FL, Elsenbroek JH, Lombard M, deBruin D (1997) Geochemical exploration for platinum-group elements in the Bushveld complex, South Africa. Miner Deposita 32:349–361

Zhulidov AV, Robarts RD, Pavlov DF, Kämäri J, Gurtovaya TY, Meriläinen JJ, Pospelov IN (2011) Long-term changes of heavy metal and sulphur concentrations in ecosystems of the Taymyr Peninsula (Russian Federation) North of the Norilsk Industrial Complex. Environ Monit Assess 181:539–553

Part II

Analytical Methods for the Determination of PGE in Biological and Environmental Matrices

Appraisal of Biosorption for Recovery, Separation and Determination of Platinum, Palladium and Rhodium in Environmental Samples

Beata Godlewska-Żyłkiewicz and Julita Malejko

Abstract The potential of metal sorption by certain types of biomass provides the basis for the development of a new approach to remove heavy metals when they are present at low concentration. Seaweeds, fungi, yeast, bacteria and other native biomaterials, such as industrial and agricultural wastes and compounds derived from plant and animal tissues (e.g. lignin, tannin, chitin and chitosan), can be used as metal sorbents. The literature review shows that in the case of biomaterials of plant and animal origin mainly basic investigation on the biosorption mechanism, kinetics and thermodynamics of biosorption process using standard solutions of platinum group elements was described. For the recovery of these metals from real effluents and waste materials different types of microorganisms were applied. Due to good sorption performance and high selectivity, microorganisms were also used in analytical application for the separation and preconcentration of metals from interfering matrix before their determination by spectrometric techniques. In this book chapter the employment of biosorption processes for removal/recovery of platinum, palladium and rhodium from wastes and the procedures of their determination in environmental samples using biosorption process and different detection techniques are presented and discussed.

1 Introduction

Extensive use of platinum group elements (PGE) in metallurgy, various chemical syntheses, electronic applications and medicine as well as in the production of catalytic converters for car engines (Matthey 2013; Zereini and Alt 2006) has resulted in increasing demand for these metals. However, the PGE refineries

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generate large volumes of wastewater which still contain considerable amounts of precious metals (Dobson and Burgess 2007; Mack et al. 2007). Additionally, frequent updating of PC computers, mobile phones and entertainment devices generates a new source of waste, named e-waste. Therefore, the development of effective methods for the removal/recovery of precious metals from a variety of waste materials became necessary for economic reasons as well as for the creation of the sustainable world. The conventional methods include pyro- and hydrometallurgical processing, chemical precipitation, solvent extraction, membrane filtration and ion exchange (Cui and Zhang 2008; Fontas et al. 2003). A new approach to remove low concentrations of precious metals from effluents is biosorption (Das 2010; Mack et al. 2007). This process of metal binding by the biomass is a very promising technology due to a low operation cost, high efficiency in detoxification of effluents and selectivity. Seaweeds, fungi, yeast, bacteria and other native biomaterials, such as industrial and agricultural wastes and compounds derived from plant and animal tissues (e.g. lignin, tannin, chitin and chitosan), have been used as metal sorbents (Das 2010; Mack et al. 2007; Park et al. 2010a; Wang and Chen 2009).

On the other hand, the growing industrial and medical use of platinum group elements causes their emission into different compartments of the environment. Analysis of airborne particulate matter, road and tunnel dust, soil, sewage sludge, urban river and lake waters, and sediment cores demonstrated that the anthropogenic activity has resulted in elevated concentrations of these elements in such samples (Jackson et al. 2010; Kalavrouziotis and Koukoulakis 2009; Rauch et al. 2000; Zereini and Alt 2000). Determination of PGE in environmental samples requires application of sensitive and selective analytical techniques, such as atomic absorption and emission spectrometry (AAS, OES) and inductively coupled plasma mass spectrometry (ICP MS). However, the application of ETAAS for the determination of Pt, Pd and Rh is sometimes limited by insufficient detection limit and occurrence of spectral interferences, which are usually caused by a not completely compensated background signal of matrix origin. ICP OES and ICP MS techniques suffer from spectral interferences arising from more abundant constituents of the sample as well (Godlewska-Żyłkiewicz 2004; Godlewska-Żyłkiewicz and Leśniewska 2006). Flow injection chemiluminescence (FI-CL) methods of Pt(IV) determination have been developed recently (Malejko et al. 2007, 2010). These methods are based on catalytic effect of analyte on the chemiluminescence reaction of luminol oxidation in alkaline medium (Malejko et al. 2007) and on quenching effect of analyte on the chemiluminescence generated by lucigenin in alkaline solution (Malejko et al. 2010). High sensitivity, low detection limits (0.03–0.7 ng mL^{-1} Pt), high sample throughput, simple and inexpensive instrumentation (no external light source is required) are the main advantages of these methods. However, the accuracy of CL determination of Pt in environmental samples is strongly affected by matrix components (other metals and organic compounds). Therefore, a separation/pre-concentration step must be introduced into the analytical procedure for PGE determination. For this purpose chemical precipitation (Alsenz et al. 2009), solvent extraction (Shampsiur et al. 2009), electrodeposition (Godlewska-Żyłkiewicz and Zaleska 2002), and solid phase extraction (Godlewska-Żyłkiewicz 2004; Myasoedova et al. 2007) have been applied. In solid phase extraction (SPE) the analytes are partitioned between a solid and a liquid phases basing on their affinity for the solid phase. Choice of an appropriate sorbent is crucial for the development of SPE methodology. The sorbent has to exhibit certain properties as sufficient selectivity and capacity, high distribution coefficients for analyte but not for matrix components, fast kinetics of sorption and elution processes as well as tolerance against high flow rate in flow procedures. The mechanisms of retention include adsorption (Ebrahimzadeh et al. 2010; Leśniewska et al. 2005; Rastegarzadeh et al. 2010), chelation (Rojas et al. 2006, 2009), ion-exchange (Krishna et al. 2009; Nakajima et al. 2009) and ion-pair formation. The most commonly used packing materials for separation of PGE are polymeric resins based on polystyrene, polystyrene-divinylbenzene or cellulose and silica gels functionalized or coated with different chelating groups (containing e.g. N, S atoms) (Godlewska-Żyłkiewicz 2004). Non-polar sorbents, based on hydrophobic polymeric phase or activated carbon, are capable of extracting low polarity PGE complexes from aqueous solutions through reverse phase sorption. The main limitation of using of commercially available sorbents for separation of PGE is the lack of selectivity, therefore in some cases the addition of masking agents to the sample solution was essential. Nowadays, the introduction of new, more selective sorbents, based on free and immobilized biomass, into the SPE methodologies is observed. Analytical applications of biosorbents for the separation and preconcentration of various metals before their determination by spectrometric techniques have been reviewed (Godlewska-Żyłkiewicz 2006; Pacheco et al. 2011).

In this chapter the employment of biosorption processes for removal/recovery of platinum, palladium and rhodium from wastes and analytical applications of biosorption for separation of trace amounts of these metals from interfering matrix of samples are described.

2 Biosorption of Metal Ions

Biosorption is a passive non-metabolically mediated process of binding of different chemical compounds by biomass (Volesky 2007). It does not depend on temperature, metabolic energy or the presence of metabolic inhibitors. It usually involves adsorption of metal ions at the cell wall via physicochemical interactions with various functional groups including carboxylate, hydroxide, amine, amide, imidazole, sulfate, and sulfhydryl. Binding is attributed to ion-exchange, adsorption, complexation, microprecipitation and crystallization processes occurring on the cell wall (Fig. 1). Often some of these mechanisms act simultaneously. Bioaccumulation is an active process in which metals are transported into the cell and

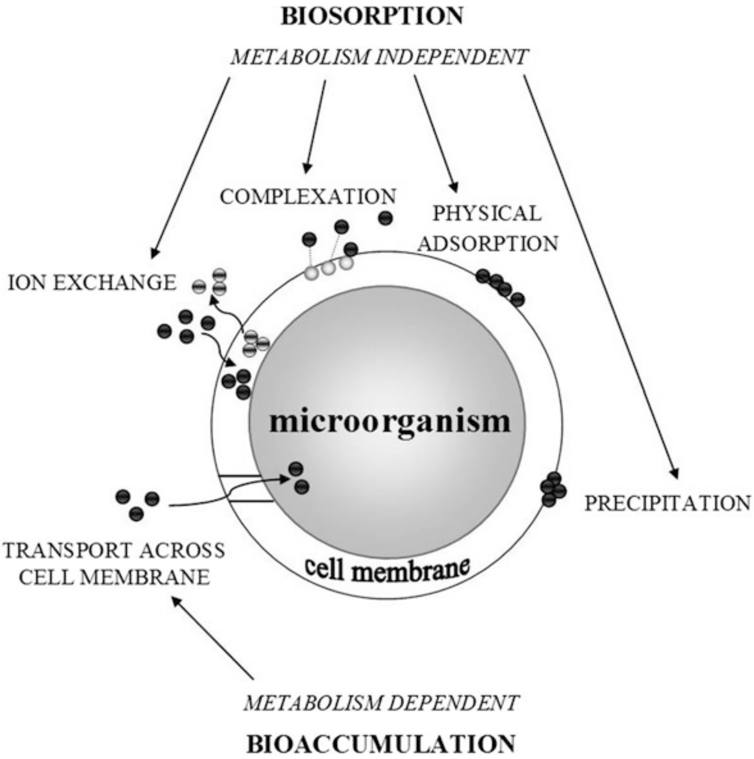

Fig. 1 Mechanisms of biosorption and bioaccumulation of metal ions by microorganisms

subsequently transformed in processes of reduction and oxidation, methylation, or precipitation. Biosorption of metals by biomass depends mainly on the type of biomaterial, principally structure and composition of its cell wall, the chemistry of the metal ion and the external parameters of the process. Among them mass of biosorbent, contact time between biomass and metal ions, temperature, solution pH and its ionic strength, and the type and content of other ions mostly influence the biosorption efficiency.

Both free and immobilized biomass could be used as biosorbent in batch and flow procedures (Park et al. 2010a). The disadvantages of batch procedures are problems with solid/liquid separation, instability of biomass in consequent cycles, the need for multiple extraction of metals that have low partition coefficients. To overcome these limitations biomass is often immobilized on solid support by covalent bonding, entrapment in a polymeric matrix or crosslinking with special reagents, e.g. glutaraldehyde, polyacrylamide or polyethyleneimine. Immobilized biomass shows better mechanical properties which enables to use such material as a filling of columns in flow procedures. Using this approach biosorbents can be easily regenerated and used multiple times.

3 Application of Inactive Biomass Derived from Plant or Animal Tissues for Biosorption of PGE

Several biosorbents have been investigated for the removal of Pt and Pd from model aqueous solutions (Table 1). Chitosan is a linear polysaccharide composed of randomly distributed β-(1–4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit) obtained from shrimp and other crustacean shells. Glutaraldehyde cross-linked chitosan and its sulfur derivatives have been studied for biosorption of Pt(IV) and Pd(II) ions from dilute solutions (Guibal et al. 1999, 2000, 2002). The glutaraldehyde cross-linking was necessary for stabilization of the chitosan in acidic pH (pH 2), optimal for sorption of both metals. Analogous chitosan derivatives namely glutaraldehyde cross-linked (GA), poly(ethyleneimine) grafted (PEI) and thiourea grafted (TDC) have been studied for sorption of platinum and palladium from bicomponent solutions by Chassary et al. (2005). Cross-linked chitosan resins chemically modified with glycine (Ramesh et al. 2008), l-lysine (Fujiwara et al. 2007) and ethylenediamine (Zhou et al. 2010) have also been used for such investigations. Generally, it was stated that anionic chlorocomplexes of Pt(IV) and Pd(II) on all studied sorbents were bound by electrostatic attractions to the positively charged amino groups. This process was simultaneously accompanied by chelation of the metal ion on sulphur containing groups on thiourea modified sorbents.

The adsorption of noble metals on different tannins containing multiple adjacent hydroxyl groups was studied by some research groups (Kim and Nakano 2005; Ma et al. 2006; Wang et al. 2005). Kim and Nakano (2005) applied tannin gel particles to Pd removal. They confirmed by XRD (X-ray diffraction) technique that the reduction of Pd(II) and crystallization of reduced Pd(0) on tannin gel network occurred. Wang et al. (2005) have found that the collagen fiber immobilized bayberry tannin exhibited high adsorption capacity to Pt(II) and Pd(II) at pH 2, even in the presence of Fe(III), Cu(II), Ni(II), and Zn(II) ions. The adsorption of Pt(IV) and Pd(II) on bayberry tannin immobilized on collagen fiber (BTICF) was also investigated by Ma et al. (2006).

Parsons et al. (2003) have used powdered leaves and stems of alfalfa (*Medicago sativa)* to study biosorption of $PtCl_6^{2-}$ and $PtCl_4^{2-}$. The process was performed for 60 min in a batch mode. The highest efficiency of biosorption was obtained at pH 2 for Pt(IV) (65%) and at pH 3 for Pt(II) (80 %). After chemical modification of biomass by esterification of carboxylic groups to methyl esters, the negative charge of cell wall decreased and the highest efficiency of biosorption of Pt(IV) (90 %) was obtained at pH 6.

Aminated lignin derivatives obtained from wood powder, containing primary amine and ethylenediamine functional groups were used for removal of Pd(II) and Pt(IV) from strong hydrochloric acid solutions (Parajuli et al. 2006), while aminated crosslinked lignophenol (prepared by immobilizing phenol with wood lignin followed by crosslinking with paraformaldehyde and chemical modification with dimethylamine) was studied for recovery of precious metals from an actual

Table 1 Parameters of biosorption process of platinum and palladium on biomaterials

Biosorbent	Biosorption conditions	Maximum sorption capacity, q_{max} (mg g^{-1})	References
Chitosan crosslinked with glutaraldehyde	Sample pH: 2, contact time: 72 h, mass of biomass: 0.01 g, temperature: 20 °C	304.1 (Pt)	Guibal et al. (2000)
Chitosan crosslinked with glutaraldehyde and grafted with thiourea	Sample pH: 2, contact time: 72 h, mass of biomass: 0.01 g, temperature: 20 °C	346.2 (Pt)	Guibal et al. (2000)
Glutaraldehyde crosslinked chitosan	Sample pH: 2.2, contact time: 96 h, mass of biomass: 0.08 g, temperature: 20 °C	287.4 (Pd)	Guibal et al. (2002)
Thiourea derivative of chitosan Rubeanic acid derivative of chitosan	Sample pH: 2.2, contact time: 96 h, mass of biomass: 0.08 g, temperature: 20 °C	277.5 (Pd) 352.0 (Pd)	Guibal et al. (2002)
Glycine modified crosslinked chitosan resin	Sample pH: 2, contact time: 2 h, mass of biomass: 0.1 g, temperature: 30 °C	122.47 (Pt) 120.39 (Pd)	Ramesh et al. (2008)
Ethylenediamine-modified magnetic chitosan	Sample pH: 2, contact time: 1 h, mass of biomass: 0.05 g, temperature: 25 °C	171 (Pt) 138 (Pd)	Zhou et al. (2010)
Collagen fiber immobilized bayberry tannin	Sample pH: 2, contact time: 48 h, mass of biomass: 0.05 g (Pt), 0.1 g (Pd), temperature: 30 °C	96.56 (Pt) 85.14 (Pd)	Wang et al. (2005)
Collagen fiber immobilized bayberry tannin	Sample pH: 3 (Pt), 4 (Pd), contact time: 60 min (Pt), 240 min (Pd), mass of biomass: 0.1 g, temperature: 30 °C;	45.8 (Pt) 33.4 (Pd)	Ma et al. (2006)
Polyamine cross-linked lignophenol	Sample pH: 0.3, contact time: 100 h, mass of biomass: 0.02 g, temperature: 30 °C	42.92 (Pt) 22.67 (Pd)	Parajuli et al. (2006)
Polyethylenediamine crosslinked lignophenol	Sample pH: 0.3, contact time: 100 h, mass of biomass: 0.02 g, temperature: 30 °C	104.56 (Pt) 40.44 (Pd)	Parajuli et al. (2006)

(continued)

Table 1 (continued)

Biosorbent	Biosorption conditions	Maximum sorption capacity, q_{max} (mg g^{-1})	References
Terrestial moss *Racomitrium lanuginosum*	Sample pH: 5, contact time: 30 min, mass of biomass: 0.1 g, temperature: 25 °C	37.2 (Pd)	Sari et al. (2009)
Cedar wood powder	Sample pH: 1, contact time: 24 h, mass of biomass: 0.01 g, temperature: 30 °C	148.99 (Pd)	Parajuli and Hirota 2009
Sulfate reducing bacteria (SRB) *Desulfovibrio desulfuricans*	Sample pH: 3, contact time: 20 min, mass of biomass: 0.0015 g, temperature: 30 °C	90 (Pt) 190 (Pd)	de Vargas et al. (2004)
Polyethylenimine (PEI)-modified *Escherichia coli*	Sample pH: extremely acidic condition, contact time: 60 min, mass of biomass: 0–1.8 g, temperature: 25 °C	108.8 (Pt)	Won et al. (2010)
Escherichia coli	Sample pH: 3, contact time: 24 h, mass of biomass: 0.09 g, temperature: 25 °C	141.1 (Pd)	Park et al. (2010b)
Polyallylamine hydrochloride modified *E. coli*	Sample pH: 3, contact time: 24 h, mass of biomass: 0.09 g, temperature: 25 °C	265.3 (Pd)	Park et al. (2010b)
Tobacco mosaic virus	Sample pH: 5–5.5, contact time: 1 h, mass of biomass: 0.038 g L^{-1}, temperature: 50 °C	368.21 (Pd)	Lim et al. (2010)
Tobacco mosaic virus-wild	Sample pH: 5–5.5, contact time: 1 h, mass of biomass: 0.038 g L^{-1}, temperature: 50 °C	312.87 (Pd)	Lim et al. (2010)

industrial solution obtained after *aqua regia* leaching of metal components in obsolete e-devices (Parajuli et al. 2009).

Recently, the biosorption potential of *Racomitrium lanuginosum* (terrestrial moss) (Sari et al. 2009) and modified (aminated) cedar wood powder (Parajuli and Hirota 2009) was studied. The adsorption capacity of *R. lanuginosum* biomass for Pd(II) was found to be 37.2 mg g^{-1} at pH 5, while for cedar wood this value was 148.99 mg g^{-1} at pH 1. The application of cedar wood for the recovery of Pd(II) from nuclear fuel wastes has been reported. Water fern *Azolla filiculoides* (grinded particles) was applied to recovery of Rh(III) from raw and pretreated (after removal of nitrogenous compounds) metal refinery wastewater (Manipura and Burgess 2008).

The biosorption conditions of PGE on sorbents of plant and animal origin are summarized in Table 1. The literature review shows that mainly basic investigation on the biosorption mechanism, kinetics and thermodynamics of biosorption process using standard solutions was described. Only few applications to removal of PGE from actual samples have been reported on such sorbents (Parajuli and Hirota 2009).

4 Application of Microorganisms for Removal of PGE

Biomaterials most widely used for removing Pt, Pd and Rh from aqueous solutions are microorganisms. Their cell wall consists of polysaccharides, proteins and lipids, which provide variety of effective sites for metal binding. Moreover, microorganisms can be used as dead or live biomass and can uptake metal ions through metabolism-independent biosorption on the cell surface and/or metabolism-dependent active bioaccumulation. Different species of bacteria, as well as yeast, fungi and virus were used for PGE removal. Among them some promising biosorbents for the recovery of precious metals from industrial effluents and leachates of spent automotive catalyst can be found. The literature on this topic is reviewed below and presented in Table 1.

Sulfate-reducing bacteria (SRB) are anaerobic microorganisms that can obtain energy by oxidizing organic compounds or molecular hydrogen (H_2) while reducing sulfate (SO_4^{2-}) to hydrogen sulfide (H_2S). Three different species of *Desulfovibrio: Desulfovibrio desulfuricans, Desulfovibrio fructosivorans* and *Desulfovibrio vulgaris* were studied as biosorbents for Pd(II) and Pt(IV) (de Vargas et al. 2004). The most promising results were obtained using *D. desulfuricans*: 90 % of total sorption was achieved in 5–15 min and the biosorption capacity at pH 3 was 190 mg g^{-1} dry biomass and 90 mg g^{-1} dry biomass for Pd and Pt, respectively. It was found that chloride ions present in the solution compete with analyte ions for active groups of microorganisms, as the biosorption of both metals decreased in the presence of NaCl concentrations above 0.1 mol L^{-1}.

The affinity of bacteria *D. desulfuricans* to Pd(II) ions (as $PdCl_4^{2-}$ and $Pd(NH_3)_4^{2+}$) was studied in the presence and the absence of the donor of electrons (formate or hydrogen) (Yong et al. 2002a, b). Biosorption of $PdCl_4^{2-}$ was most effective (70 %) at pH 4, while biosorption of $Pd(NH_3)_4^{2+}$ was lower (20–30 %) and independent on pH. In the presence of formate up to 100 % of Pd(II) bioreduction to Pd(0) was achieved within 5 min at pH 7 and 30 min at pH 3. In the presence of hydrogen the maximum rate of Pd(II) reduction was seen at pH 3–7. The potential of *D. desulfuricans* for the recovery of Pd from spent automotive catalyst leachates and industrial processing wastewater was investigated. Other studies have shown that Pt(IV) and Rh(III) ions can be also transformed to elemental form by SRB in the presence of H_2 as a donor of electrons (Ngwenya and Whiteley 2006; Rashamuse and Whiteley 2007). Bioreduction of Pt(IV) was most efficient at pH 7, while of Rh(III) at pH range 4–7. Sorption capacity of bacteria was 4 mg g^{-1} for Pt(IV) and 66 mg g^{-1} for Rh(III).

The reduction of Pt(IV) to Pt(0) by bacteria *Shewanella algae* was described by Konishi et al. (2007). After 60 min contact time at pH 7 in the presence of sodium lactate as the donor of electrons 10-fold decrease in concentration of Pt(IV), due to the formation of Pt(0) nanoparticles, was observed. Nanoparticles of Pt(0) and Pd (0) were also formed during interaction of filamentous cyanobacteria *Plectonema boryanum* with $PtCl_4$ and $PdCl_2$ (Lengke et al. 2006, 2007). These studies offer an alternative method to standard abiotic chemical methods for the synthesis of platinum and palladium nanoparticles. Biomass-supported Pt(0) or Pd(0) nanoparticles can be used as catalysts in the remediation of contaminated environment.

The recovery of Pt by a poly(ethyleneimine) (PEI) modified biomass, prepared by attaching PEI onto the surface of inactive *Escherichia coli* biomass (obtained from fermentation industry) was reported by Won et al. (2010). The maximum Pt (IV) uptake of PEI-modified biomass was enhanced up to 108.8 mg g^{-1} compared to 21.4 mg g^{-1} of the raw biomass. Metallic form of platinum was recovered from biomass by incineration with recovery efficiency from ash of over 98.7 %. This sorbent was tested for the removal of analyte from wastewater collected from an industrial laboratory. Biosorbent obtained by cross-linking of waste biomass *E. coli* with polyallylamine hydrochloride (PAH) was investigated for the recovery of Pd (II) and Pt(IV) from aqueous solution (Mao et al. 2010; Park et al. 2010b). The sorption performance of the PAH-modified biomass was greater than that of the raw *E. coli*. The maximum uptakes of Pd(II) and Pt(IV) were 265.3 mg g^{-1} (at pH 3) and 348.8 mg g^{-1} (at pH 2), respectively. The researchers concluded that PAH-modified *E. coli* is a useful and cost-effective biosorbent for the recovery of PGE from metal refining processes.

Pd(II) biosorption on the genetically-modified Tobacco mosaic virus (TMV) has been investigated by Lim et al. (2010). The insertion of the additional sulfhydryl groups on the TMV surface improved the loading capacity of Pd(II) ions compared to that obtained on the wild-type TMV.

Saccharomyces sp. is perhaps the most important yeast owing to its use for the biofuel, bakery and beverage industries or for the production of biotechnological products (e.g. enzymes, pharmaceutical products). Yeast cells, which may be obtained in large quantities, are an inexpensive source of biomass. Mack et al. (2008) have studied a kinetic of the sorption of Pt(IV) by immobilized *Saccharomyces cerevisiae* biomass. They found that the efficiency of Pt retention depends on the initial metal concentration, mass of biosorbent and temperature of solution. They observed rapid Pt(IV) removal (app. 70 %) at pH 1.5 during first 5 min, after which it slowed significantly as it reached equilibrium. The initial rapid stage was attributed to an initial non-specific sorption of Pt(IV) ions due to electrostatic attractions between protonated sorbent and platinum anions. The second stage was identified as a chemical sorption such as covalent bonding or microprecipitation. Other studies have shown that *S. cerevisiae* immobilised using polyethyleneimine and glutaraldehyde is a suitable biosorbent, capable of high uptake of Pt(IV) (150–170 mg g^{-1}) at low pH (below 2) (Mack et al. 2011). The potential of immobilised yeast for the recovery of Pt from PGE refinery wastewater was investigated. The applicability of the biosorption process was limited by high content of inorganic ions and complex speciation of platinum in wastewater.

The study on biosorption of platinum on fungi was carried out by Moore et al. (2008). Uptake efficiency at pH 2–3 within 48 h remained at 85 % for initial platinum ion concentrations. This work demonstrated the potential for fungal treatment of process wastewater.

5 Analytical Application of Microorganisms for Separation/Preconcentration of PGE from Environmental Samples

Only several applications of microorganisms for separation of PGE from interfering matrix have been published so far. Algae *Chlorella vulgaris,* yeast *Saccharomyces cerevisiae* and fungi *Aspergillus sp.* were applied to selective separation and determination of Pt(IV) and Pd(II) by atomic absorption spectrometry (Dziwulska et al. 2004; Godlewska-Żyłkiewicz 2003; Godlewska-Żyłkiewicz and Kozłowska 2005; Godlewska-Żyłkiewicz 2008; Godlewska-Żyłkiewicz et al. 2008; Woińska and Godlewska-Żyłkiewicz 2011) and flow injection chemiluminescence (Godlewska-Żyłkiewicz et al. 2007, 2008; Malejko et al. 2010, 2012) in environmental samples (Table 2).

Godlewska-Żyłkiewicz (2003) reported the binding of Pt(IV) and Pd(II) by free cells of baker's yeast *S. cerevisiae* and algae *C. vulgaris.* The highest retention of Pt (IV) and Pd(II) on yeast biomass was obtained at pH range from 1.4 to 4.1 and from 1.4 to 2.2, respectively. Biosorption of Pt(IV) and Pd(II) on algae was effective in very narrow range of pH from 0.6 to 1.9. The palladium retention on algae cells was almost quantitative (95 %) within first 25 min, however the systematic increase of platinum retention was observed with extension of the contact time up to 150 min (71 % sorption). Usually, pH-dependent binding signifies interactions via an ion-exchange mechanism, but in acidic solutions Pt and Pd occur mostly in anionic form while functional groups of the cell wall are protonated. This suggests that binding is also consistent with electrostatic forces, where at low pH, surface charge is positive and aids in negatively charged ion binding. The differing pH profiles obtained from the *C. vulgaris* and *S. cerevisiae* were attributed to dissimilar binding mechanisms for algae and yeast with respect to functional group content and involvement.

Considering these results, metabolically inactive free cells of yeast *S. cerevisiae* were used for separation of palladium from environmental samples (Godlewska-Żyłkiewicz 2008). Biosorption process was performed in batch mode for 45 min at pH 2.0–2.5. After centrifugation the solution containing thiourea (0.3 mol L^{-1}),

Table 2 Analytical applications of biosorption process on microorganisms for the separation/preconcentration of Pt(IV) and Pd(II) prior to their determination in environmental samples by ETAAS and FI-CL methods

Biosorbent	Biosorption efficiency (%) (optimal conditions of sorption)	Sorption capacity (μg g^{-1})	Recovery (%) (optimal conditions of desorption)	Detection technique LOD (ng mL^{-1})	Sample	References
Algae *C. vulgaris*	71.4 ± 2.9 (Pt) 95.1 ± 2.2 (Pd) (batch mode, sample pH: 1.8 (Pt), 1.5–1.6 (Pd), contact time: 120 min (Pt), 30 min (Pd))	6.7 (Pd)	–	ETAAS	–	Godlewska-Żyłkiewicz (2003)
Algae *C. vulgaris* immobilized on silica gel	93.3 ± 1.6 (Pt) 96.6 ± 1.1 (Pd) (flow mode, sample pH: 1.6)	–	87.7 ± 1.7 (Pt) 96.8 ± 1.1 (Pd) (eluent: 0.3 mol L^{-1} TU + 1 mol L^{-1} HCl, flow rate: 0.25 mL min^{-1})	ETAAS 0.4 (Pt) 0.8 (Pd)	Tap water, wastewater	
Algae *C. vulgaris* immobilized on Cellex-T resin	95.2 ± 0.4 (Pt) 99.3 ± 0.9 (Pd) (flow mode, sample pH: 1.5–1.8)	25 (Pt) 13.3 (Pd)	93.4 ± 2.4 (Pt) 94.9 ± 4.1 (Pd) (eluent: 0.3 mol L^{-1} TU + 1 mol L^{-1} HCl, flow rate: 0.25 mL min^{-1})	ETAAS 0.2 (Pt) 0.096 (Pd)	Tap water, wastewater, grass	Dziwulska et al. (2004)
			98.5 ± 4.0 (Pt) (eluent: 3.0 mol L^{-1} NaCl, flow rate: 2.2 mL min^{-1})	luminol-based FI-CL 0.057 (Pt)	River water	Godlewska-Żyłkiewicz et al. (2007)
			98.9 ± 2.8 (Pt) (eluent: 0.75 mol L^{-1} NaCl, flow rate: 2.7 mL min^{-1})	lucigenin-based FI-CL 0.1 (Pt)	BCR-723, river water, road dust	Malejko et al. (2010)

(continued)

Table 2 (continued)

Biosorbent	Biosorption efficiency (%) (optimal conditions of sorption)	Sorption capacity (μg g^{-1})	Recovery (%) (optimal conditions of desorption)	Detection technique LOD (ng mL^{-1})	Sample	References
Yeast *S. cerevisiae*, active cells	78.3 ± 1.2 (Pt) 98.9 ± 0.7 (Pd) (batch mode, sample pH: 1.8–2.2 (Pt), 1.4–1.6 (Pd), contact time: 60 min (Pt), 30 min (Pd))	0.8 (Pt) 12 (Pd)	–	ETAAS	–	Godlewska-Żyłkiewicz (2003)
Yeast *S. cerevisiae*, inactive cells	90.1 ± 0.7 (Pd) (batch mode, sample pH: 2.0–2.5, contact time: 45 min)	21 (Pd)	102.9 ± 11.2 (Pd) (desorption by 0.3 mol L^{-1} TU + 1 mol L^{-1} HCl + 0.5 % Triton X-100)	Slurry sampling ETAAS 1 (Pd)	Tap water, road dust	Godlewska-Żyłkiewicz (2008)
Yeast *S. cerevisiae* immobilized in calcium alginate	90.3 ± 2.5 (Pt) 81.8 ± 4.8 (Pd) (flow mode, sample pH: 1.8 (Pt), 1.0–1.5 (Pd)	24 (Pt) 10 (Pd)	90.4 ± 3.4 (Pt) 101.0 ± 4.6 (Pd) (eluent: 0.2 mol L^{-1} TU + 0.25 mol L^{-1} HCl (Pt), 0.3 mol L^{-1} TU + 0.25 mol L^{-1} HCl (Pd), flow rate: 0.75 mL min^{-1} (Pt), 1.0 mL min^{-1} (Pd)	ETAAS 6 (Pt) 1.41 (Pd)	SARM-7, tap and river water, road dust, grass	Godlewska-Żyłkiewicz and Kozłowska (2005), Godlewska-Żyłkiewicz et al. (2008)
			83.0 ± 2.8 (Pt) (eluent: 3.0 mol L^{-1} NaCl, flow rate: 2.0 mL min^{-1}),	luminol-based FI-CL 0.15 (Pt)	River water	Godlewska-Żyłkiewicz et al. (2008)

(continued)

Table 2 (continued)

Biosorbent	Biosorption efficiency (%) (optimal conditions of sorption)	Sorption capacity (μg g^{-1})	Recovery (%) (optimal conditions of desorption)	Detection technique LOD (ng mL^{-1})	Sample	References
Fungi *Aspergillus sp.* immobilized on Cellex-T resin	99.4 ± 0.5 (Pt) 99.6 ± 0.5 (Pd) (flow mode, sample pH: 1.0)	470 (Pt) 1,240 (Pd)	93.0 ± 3.0 (Pt) 93.0 ± 5.1 (Pd) (eluent: 0.3 mol L^{-1} TU + 0.25 mol L^{-1} HCl, flow rate: 0.6 mL min^{-1} (Pt), 1.0 mL min^{-1} (Pd)	ETAAS 0.020 (Pt) 0.012 (Pd)	BCR-723, SARM-76, anode slime, road dust	Woińska and Godlewska-Żyłkiewicz (2011)
			92.0 ± 8.8 (Pt) (eluent: 5.0 mol L^{-1} NaCl, flow rate: 2.2 mL min^{-1})	luminol-based FI-CL 0.02 (Pt)	River water, road run-off, wastewater	Malejko et al. (2012)

TU — thiourea; BCR-723 — certified reference material of tunnel dust; SARM-7, SARM-76 — certified reference materials of platinum ore

HCl (1 mol L^{-1}) and Triton X-100 (0.5 %) was added to biomass and stirred for 10 min in order to desorb the analyte. Palladium content was determined by slurry sampling ETAAS. The method was successfully applied to the separation of Pd(II) from tap water. For the analysis of more complicated samples, such as road dust, the initial separation of interfering ions on cation-exchange resin Dowex 50 WX-8 was performed.

A dynamic SPE procedures using yeast *S. cerevisiae* immobilized in calcium alginate beads were proposed for the determination of Pd by ETAAS (Godlewska-Żyłkiewicz and Kozłowska 2005) and Pt by ETAAS and FI-CL methods (Godlewska-Żyłkiewicz et al. 2008) in environmental samples. It was found that efficiency of Pd(II) biosorption was maximal (81 %) at pH range from 1.0 to 2.5, while efficiency of Pt(IV) biosorption was constant (87–93 %) in the wide range of pH 1.5–6.5 and decreased to 60 % at less and more acidic solutions. Because most of metal ions bind to cell surface of microorganisms at pH range from 5 to 8, the biosorption of Pt(IV) and Pd(II) from real samples was performed at pH 1.8 and pH 1.0–1.5, respectively. Biosorption of Pt(IV) on yeast immobilized in calcium alginate was more effective than on free cells, but the effect of immobilization was opposite for palladium (Godlewska-Żyłkiewicz 2003). Quantitative recoveries of metals were obtained with acidic solutions of thiourea during Pd and Pt determination by ETAAS (Godlewska-Żyłkiewicz and Kozłowska 2005; Godlewska-Żyłkiewicz et al. 2008) and with 3 mol L^{-1} NaCl solution during Pt determination by FI-CL method (Godlewska-Żyłkiewicz et al. 2008). Sorption capacity of sorbent was 24 μg g^{-1} for Pt and 10 μg g^{-1} for Pd. Prepared beads were used for 40 subsequent sorption-desorption cycles. The detection limits of the ETAAS methods were 6 ng mL^{-1} for Pt and 1.41 ng mL^{-1} (7 ng g^{-1} for real sample) for Pd. The interference studies showed that the efficiency of Pd(II) (50 ng mL^{-1}) retention decreased by 15 % in the presence of Cr(III) at concentration above 5 μg mL^{-1}, and by 20 % in the presence of Ni(II) and Fe(III) at concentrations above 50 μg mL^{-1} and 100 μg mL^{-1}, respectively. Acceptable concentrations of the interfering ions in ETAAS determination of 75 ng mL^{-1} Pt(IV) were: 5 μg mL^{-1} Cu(II), 50 μg mL^{-1} Fe(III) and Cr(III), 100 μg mL^{-1} Pd(II), 500 μg mL^{-1} Zn(II) and 1,000 μg mL^{-1} Pb (II). The accuracy of SPE-ETAAS procedures was confirmed by the analysis of certified reference material (platinum ore SARM-7). Developed procedures were applied to the determination of Pt and Pd in river water, grass and road dust. The FI-CL method of determination of Pt is characterized by lower detection limit (0.15 ng mL^{-1}) than ETAAS method, but due to its poorer selectivity can be used only for the analysis of simple matrices, such as river waters.

Algae *C. vulgaris* immobilized on silica gel and cellulose anion-exchange resin (Cellex-T) were also studied as a Pt and Pd biosorbents for separation/preconcentration of metal ions prior to their ETAAS (Dziwulska et al. 2004; Godlewska-Żyłkiewicz 2003) and FI-CL (Godlewska-Żyłkiewicz et al. 2007; Malejko et al. 2010) determination in environmental samples. The biosorption at optimum pH 1.5–1.8 was 93.3–99.3 % for both metals. It is worth to notice that efficiency of Pt(IV) biosorption increased by 20 % on immobilized algae in comparison to free cells. The mechanism of biosorption is considered to be electrostatic, where at low pH the overall surface charge on the biomass is positive, assisting in the approach of negatively charged Pt and Pd ions ($PtCl_6^{2-}$, $PdCl_4^{2-}$) through electrostatic forces. It was also suggested that functional groups containing nitrogen and/or sulfur atoms from protonated amine or imidazole as well as thiol groups, might be responsible for biosorption. Quantitative elution of platinum and palladium from both sorbents before their ETAAS detection was obtained with 0.3 mol L^{-1} thiourea in 1 mol L^{-1} HCl (Dziwulska et al. 2004; Godlewska-Żyłkiewicz 2003). Quantitative recovery of Pt(IV) from algae *C. vulgaris* immobilized on Cellex-T can be also obtained by using sodium chloride solution. This eluent was applied for desorbing of platinum before its luminol-based (Godlewska-Żyłkiewicz et al. 2007) and lucigenin-based (Malejko et al. 2010) FI-CL determination. The biosorption efficiency of studied metals on the sorbents was constant during 20 successive cycles. The sorption capacity for Pt(IV) was 25 μg g^{-1} while for Pd(II) was 13.3 μg g^{-1} (Dziwulska et al. 2004).

In many cases introduction of the separation step into analytical procedure allows for preconcentration of determined metals. Higher sensitivity of the method as well as lower limits of detection of Pt (0.4 ng mL^{-1}) and Pd (0.8 ng mL^{-1}) were obtained after the biosorption step on algae *C. vulgaris* immobilized on silica gel compared to these obtained by the direct determination of analytes by ETAAS method (Godlewska-Żyłkiewicz 2003). Limits of detection of Pt and Pd obtained by the SPE procedure using algae immobilized on Cellex-T resin followed by ETAAS detection were even lower and equal to 0.2 ng mL^{-1} for Pt and 0.096 ng mL^{-1} for Pd (Dziwulska et al. 2004). The detection limits of Pt(IV) achieved by FI-CL methods after analyte preconcentration on algae *C. vulgaris* immobilized on Cellex-T were 0.057 ng mL^{-1} for luminol-based method (Godlewska-Żyłkiewicz et al. 2007) and 0.1 ng mL^{-1} for lucigenin-based method (Malejko et al. 2010), and were 2.5-fold and 7-fold lower compared to the direct measurements.

The effect of the presence of other metal ions (Na(I), Zn(II), Ni(II), Co(II), Cu (II), Mn(II) and Fe(III)) on the retention of Pd(II) on algae immobilized on silica gel (Godlewska-Żyłkiewicz 2003) and on the retention of Pt(IV) on algae immobilized on Cellex-T (Dziwulska et al. 2004) was investigated by ETAAS method. It was confirmed that the evaluated SPE procedures are very selective toward studied metals. The more significant effect on retention of palladium and platinum was observed only in the presence of Co(II) and Fe(III) ions (at their concentration of 100 μg mL^{-1}) and Fe(III) and Zn(II) ions (at their concentration of 10 μg mL^{-1}), respectively. The most significant interfering effect on luminol-based FI-CL determination of Pt(IV) after its separation on algae *C. vulgaris* immobilized on Cellex-T was observed in the presence of Co(II), Pd(II), Cr(III) and Cr(VI) ions (Godlewska-Żyłkiewicz et al. 2007). Considerably less susceptible to interference caused by the presence of other metal ions has proved to be a FI-CL method of Pt (IV) determination based on the quenching effect of the analyte on lucigenin chemiluminescence (Malejko et al. 2010). The Pt(II) and Rh(III) ions disturb the determination of Pt(IV), if their concentrations are more than 2,500 times that of analyte, whereas Pd(II) ions interfere when Pd(II)/Pt(IV) concentration ratio is above 5,000. The ETAAS and FI-CL methods were applied to the determination of

Pt and Pd in tap and river water, wastewater, grass cultivated on PGE containing nutrient, and road dust.

A SPE procedure based on biosorption of Pt(IV) and Pd(II) on fungi *Aspergillus sp.* immobilized on Cellex-T resin was also proposed for the preconcentration/separation of metals prior to their determination by ETAAS (Woińska and Godlewska-Żyłkiewicz 2011) and luminol-based FI-CL method (Malejko et al. 2012). The Pt(IV) and Pd(II) ions were quantitatively and selectively retained on the biosorbent from acidic solution of pH 1 and subsequently eluted with 0.25 mol L^{-1} thiourea solution in 0.3 mol L^{-1} HCl during Pd and Pt determination by ETAAS and with 5 mol L^{-1} NaCl solution during Pt determination by FI-CL method. The capacity of biosorbent was 470 μg g^{-1} for Pt and 1,240 μg g^{-1} for Pd, which is much higher as compared to immobilized yeast (Godlewska-Żyłkiewicz and Kozłowska 2005; Godlewska-Żyłkiewicz et al. 2008) and algae (Dziwulska et al. 2004). The biosorbent is characterized by good stability—it could be used for 48 subsequent retention/elution cycles without significant change in its sorption performance. The limit of detection of Pd achieved by the ETAAS method was 0.012 ng mL^{-1}. The LOD of Pt was the same for ETAAS and FI-CL methods and was equal to 0.020 ng mL^{-1}. The achieved detection limits are lower than that obtained after biosorption of Pt(IV) and Pd(II) on immobilized yeast and algae. Among the tested biosorbents (immobilized *C. vulgaris, S. cerevisiae* and *Aspergillus sp.*), the immobilized fungi showed the greatest capability to the selective retention of Pt(IV) and Pd(II) ions in the presence of other metal ions. The validation of the ETAAS method was performed by the analysis of certified reference materials: SARM-76 (platinum ore) and BCR-723 (tunnel dust). The SPE-ETAAS procedure was applied to the determination of Pt and Pd in road dust samples (Woińska and Godlewska-Żyłkiewicz 2011). Selectivity of the SPE procedure ensured effective separation of Pt(IV) from interfering matrix and accurate FI-CL determination of platinum in river water, road run-off water and municipal wastewater (Malejko et al. 2012).

6 Conclusions

Biosorption and bioaccumulation of platinum, palladium and rhodium has received increasing attention over the past decade. Two trends in application of these processes can be distinguished. First, the researchers have focused on searching of new biomaterials which can be exploited for the recovery of PGE from waste materials, as well as in the biosynthesis of Pt and Pd nanoparticles in order to obtain highly active “bionanocatalysts”. The literature in this field is rather scarce. This could be due to high economic value of such data.

Second trend is the application of microorganisms in analytical chemistry for the separation and preconcentration of platinum and palladium prior to their determination by spectrometric techniques (ETAAS and CL). Biosorbents, including free and immobilized biomass (algae *Chlorella vulgaris,* yeast *Saccharomyces* *cerevisiae* and fungi *Aspergillus sp.*), have proved to be an attractive alternative to the traditional, commercially available sorbents. Due to their good sorption performance and high selectivity, it was possible to determine traces amounts of platinum and palladium in complex environmental samples. The obtained concentrations of these metals in such samples are given in the chap. "On the Underestimated Factors Influencing the Accuracy of Determination of Pt and Pd by Electrothermal Atomic Absorption Spectrometry in Road Dust Samples".

References

Alsenz H, Zereini F, Wiseman CLS, Puttmann W (2009) Analysis of palladium concentrations in airborne particulate matter with reductive co-precipitation, He collision gas, and ID-ICP-Q-MS. Anal Bioanal Chem 395:1919–1927

Chassary P, Vincent T, Marcano JS, Macaskie LE, Guibal E (2005) Palladium and platinum recovery from bicomponent mixtures using chitosan derivatives. Hydrometallurgy 76:131–147

Cui J, Zhang L (2008) Metallurgical recovery of metals from electronic waste: a review. J Hazard Mat 158:228–256

Das N (2010) Recovery of precious metals through biosorption—a review. Hydrometallurgy 103:180–189

de Vargas I, Macaskie LE, Guibal E (2004) Biosorption of palladium and platinum by sulfate-reducing bacteria. J Chem Technol Biotechnol 79:49–56

Dobson RS, Burgess JE (2007) Biological treatment of precious metal refinery wastewater: a review. Miner Eng 20:519–532

Dziwulska U, Bajguz A, Godlewska-Żyłkiewicz B (2004) The use of algae *Chlorella vulgaris* immobilized on Cellex-T support for separation/preconcentration of trace amounts of platinum and palladium before GFAAS determination. Anal Lett 37:2189–2203

Ebrahimzadeh H, Tavassoli N, Amini MM, Fazaeli Y, Abedi H (2010) Determination of very low levels of gold and palladium in wastewater and soil samples by atomic absorption after preconcentration on modified MCM-48 and MCM-41 silica. Talanta 81:1183–1188

Fontas C, Salvago V, Hidalgo M (2003) Selective enrichement of palladium from spent automotive catalyst by using a liquid membrane system. J Membr Sci 223:39–48

Fujiwara K, Ramesh A, Maki T, Hasegawa H, Ueda K (2007) Adsorption of platinum(IV), palladium(II) and gold(III) from aqueous solutions on l-lysine modified crosslinked chitosan resin. J Hazard Mat 146:39–50

Godlewska-Żyłkiewicz B, Zaleska M (2002) Preconcentration of palladium in a flow-through electrochemical cell for determination by graphite furnace atomic absorption spectrometry. Anal Chim Acta 462:305–312

Godlewska-Żyłkiewicz B (2003) Biosorption of platinum and palladium for their separation/preconcentration prior to graphite furnace atomic absorption spectrometric determination. Spectrochim Acta B 58:1531–1540

Godlewska-Żyłkiewicz B (2004) Preconcentration and separation procedures for the spectrochemical determination of platinum and palladium. Microchim Acta 147:189–210

Godlewska-Żyłkiewicz B, Kozłowska M (2005) Solid phase extraction using immobilized yeast Saccharomyces cerevisiae for determination of palladium in road dust. Anal Chim Acta 539:61–67

Godlewska-Żyłkiewicz B (2006) Microorganisms in inorganic chemical analysis. Anal Bioanal Chem 384:114–123

Godlewska-Żyłkiewicz B, Leśniewska B (2006) Sources of error and their elimination for spectrometric determination of palladium in environmental samples. In: Zereini F, Alt F (eds)

Palladium emissions in the environment. Analytical methods, environmental assessment and health effects. Springer, Berlin, pp 97–109

Godlewska-Żyłkiewicz B, Malejko J, Hałaburda P, Leśniewska B, Kojło A (2007) Separation of matrix by means of biosorption for flow-injection chemiluminescent determination of trace amounts of Pt(IV) in natural waters. Microchem J 85:314–320

Godlewska-Żyłkiewicz B (2008) Slurry sampling electrothermal atomic absorption spectrometric determination of palladium in water using biosorption with inactive baker's yeast *Saccharomyces cerevisiae*. Int J Environ Pollut 33:1–11

Godlewska-Żyłkiewicz B, Malejko J, Leśniewska B, Kojło A (2008) Assessment of immobilized yeast for the separation and determination of platinum in environmental samples by flow-injection chemiluminescence and electrothermal atomic absorption spectrometry. Microchim Acta 163:327–334

Guibal E, Larkin A, Vincent T, Tobin JM (1999) Chitosan sorbents for platinum sorption from dilute solutions. Ind Eng Chem Res 38:4011–4022

Guibal E, Vincent T, Mendoza RN (2000) Synthesis and characterization of a thiourea derivative of chitosan for platinum recovery. J Appl Polym Sci 75:119–134

Guibal E, Von Offenberg Sweeney N, Vincent T, Tobin JM (2002) Sulfur derivatives of chitosan for palladium sorption. React Funct Polym 50:149–163

Jackson MT, Richard HM, Samson J (2010) Platinum-group elements in sewage sludge and incinerator ash in the UK: assessment of PGE sources and mobility in cities. Sci Total Environ 408:1276–1285

Kalavrouziotis IK, Koukoulakis PH (2009) The environmental impact of the platinum group elements (Pt, Pd, Rh) emitted by the automobile catalyst converters. Water Air Soil Pollut 196:393–402

Kim YH, Nakano Y (2005) Adsorption mechanism of palladium by redox within condensed-tannin gel. Water Res 39:1324–1330

Konishi Y, Ohno K, Saitoh N, Nomura T, Nagamine S, Hishida H, Takahashi Y, Uruga T (2007) Bioreductive deposition of platinum nanoparticles on the bacterium *Shewanella algae*. J Biotechnol 128:648–653

Krishna MVB, Ranjit M, Chandrasekaran K, Karunasagar D (2009) On-line preconcentration and recovery of palladium from waters using polyaniline (PANI) loaded in mini-column and determination by ICP-MS; elimination of spectral interferences. Talanta 79:1454–1463

Lengke MF, Fleet ME, Southam G (2006) Synthesis of platinum nanoparticles by reaction of filamentous cyanobacteria with platinum(IV)-chloride complex. Langmuir 22:7318–7323

Lengke MF, Fleet ME, Southam G (2007) Synthesis of palladium nanoparticles by reaction of filamentous cyanobacterial biomass with a palladium(II) chloride complex. Langmuir 23:8982–8987

Leśniewska B, Godlewska I, Godlewska-Żyłkiewicz B (2005) The study of applicability of dithiocarbamate-coated fullerene C_{60} for preconcentration of palladium for graphite furnace atomic absorption spectrometric determination in environmental samples. Spectrochim Acta B 60:377–384

Lim J-S, Kim S-M, Lee S-Y, Stach EA, Culver JN, Harris MT (2010) Quantitative study of Au(III) and Pd(II) ion biosorption on genetically engineered Tobacco mosaic virus. J Colloid Interface Sci 342:455–461

Ma HW, Liao XP, Liu X, Shi B (2006) Recovery of platinum(IV) and palladium(II) by bayberry tannin immobilized collagen fiber membrane from water solution. J Membr Sci 278:373–380

Mack C, Wilhelmi B, Duncan JR, Burgess JE (2007) Biosorption of precious metals. Biotechnol Adv 25:264–271

Mack CL, Wilhelmi B, Duncan JR, Burgess JE (2008) A kinetic study of the recovery of platinum ions from an artificial aqueous solution by immobilized *Saccharomyces cerevisiae* biomass. Miner Eng 21:31–37

Mack CL, Wilhelmi B, Duncan JR, Burgess JE (2011) Biosorptive recovery of platinum from platinum group metal refining wastewaters by immobilised *Saccharomyces cerevisiae*. Water Sci Technol 63:149–155

Malejko J, Milewska R, Leśniewska B, Godlewska-Żyłkiewicz B, Kojło A (2007) On the effect of hydrogen peroxide on the flow-injection determination of platinum based on luminol chemiluminescent reaction. Anal Lett 40:961–973

Malejko J, Godlewska-Żyłkiewicz B, Kojło A (2010) A novel flow-injection metod for the determination of Pt(IV) in environmental samples based on chemiluminescence reaction of lucigenin and biosorption. Talanta 81:1719–1724

Malejko J, Szygałowicz M, Godlewska-Żyłkiewicz B, Kojło A (2012) Sorption of platinum on immobilized microorganisms for its on-line preconcentration and chemiluminescent determination in water samples. Microchim Acta 176:429–435

Manipura A, Burgess JE (2008) Biological nitrogenous compound removal and subsequent rhodium recovery from simulated metal refinery wastewater. Miner Eng 21:652–659

Mao J, Lee SY, Won SW, Yun Y-S (2010) Surface modified bacterial biosorbent with poly (allylamine hydrochloride): Development using response surface methodology and use for recovery of hexachloroplatinate(IV) from aqueous solution. Water Res 44:5919–5928

Matthey (2013) www.matthey.com/whatwedo/productsandtechnologies/. Accessed 29 Act 2013

Moore BA, Duncan JR, Burgess JE (2008) Fungal bioaccumulation of copper, nickel, gold and platinum. Miner Eng 21:55–60

Myasoedova GV, Mokhodoeva OB, Kubrakova IV (2007) Trends in sorption preconcentration combined with noble metal determination. Anal Sci 23:1031–1039

Nakajima J, Ohno M, Chikama K, Seki T, Oguma K (2009) Determination of trace of palladium in stream sediment and auto catalyst by FI-ICP-OES using on-line separation and preconcentration with QuadraSil TA. Talanta 79:1050–1054

Ngwenya N, Whiteley CG (2006) Recovery of rhodium(III) from solutions and industrial wastewaters by a sulfate-reducing bacteria consortium. Biotechnol Prog 22:1604–1611

Pacheco PH, Gil RA, Cerutti SE, Smichowski P, Martinez LD (2011) Biosorption: A new rise for elemental solid phase extraction methods. Talanta 85:2290–2300

Parajuli D, Kawakita H, Inoue K, Funaoka M (2006) Recovery of gold(III), palladium(II), and platinum(IV) by aminated lignin derivatives. Ind Eng Chem Res 45:6405–6412

Parajuli D, Khunathai K, Raj Adhikari Ch, Inoue K, Ohto K, Kawakita H, Funaoka M, Hirota K (2009) Total recovery of gold, palladium, and platinum using lignophenol derivative. Miner Eng 22:1173–1178

Parajuli D, Hirota K (2009) Recovery of palladium using chemically modified cedar wood powder. J Colloid Interf Sci 338:371–375

Park D, Yun YS, Park JM (2010a) The past, present and future trends of biosorption. Biotechnol Bioprocess Eng 15:86–102

Park J, Won SW, Mao J, Kwak IS, Yun Y-S (2010b) Recovery of Pd(II) from hydrochloric solution using polyallylamine hydrochloride-modified *Escherichia coli* biomass. J Hazard Mater 181:794–800

Parsons JG, Gardea-Torresdey JL, Tiemann KJ, Gamez G (2003) Investigation of trace level binding of $PtCl_6$ and $PtCl_4$ to alfalfa biomass (*Medicago sativa*) using Zeeman graphite furnace atomic absorption spectrometry. Anal Chim Acta 478:139–145

Ramesh A, Hasegawa H, Sugimoto W, Maki T, Ueda K (2008) Adsorption of gold(III), platinum (IV) and palladium(II) onto glycine modified crosslinked chitosan resin. Bioresour Technol 99:3801–3809

Rashamuse KJ, Whiteley CG (2007) Bioreduction of Pt(IV) from aqueous solution using sulphate-reducing bacteria. Appl Microbiol Biotechnol 75:1429–1435

Rastegarzadeh S, Pourreza N, Kiasat AR, Yahyavi H (2010) Selective solid phase extraction of palladium by adsorption of its 5(p-dimethylaminobenzylidene)rhodanine complex on silica-PEG as a new adsorbent. Microchim Acta 170:135–140

Rauch S, Morrison GM, Motelica-Heino M, Donald OFX, Muris M (2000) Elemental association and fingerprints of traffic-related metals in road sediments. Environ Sci Technol 33:3119–3123

Rojas FS, Ojeda CB, Pavón JMC (2006) Automated on-line separation preconcentration system for palladium determination by graphite furnace atomic absorption spectrometry and its application to palladium determination in environmental and food samples. Talanta 70:979–983

Rojas FS, Ojeda CB, Pavón JMC (2009) Simultaneous determination of palladium and rhodium using on-line column enrichment and electrothermal atomic absorption spectrometric detection. J Anal Chem 64:241–246

Sari A, Durali M, Tuzen M, Soylak M (2009) Biosorption of palladium(II) from aqueous solution by moss (*Racomitrium lanuginosum*) biomass: Equilibrium, kinetic and thermodynamic studies. J Hazard Mat 162:874–879

Shampsiur M, Ramezani M, Sadeghi M (2009) Preconcentration and determination of ultra trace amounts of palladium in water samples by dispersive liquid-liquid microextraction and graphite furnace atomic absorption spectrometry. Microchim Acta 166:235–242

Volesky B (2007) Biosorption and me. Water Res 41:4017–4029

Wang J, Chen C (2009) Biosorbents for heavy metals removal and their future. Biotechnol Adv 27:195–226

Wang R, Liao X, Shi B (2005) Adsorption behaviors of Pt(II) and Pd(II) on collagen fibre immobilized bayberry tannin. Ind Eng Chem Res 44:4221–4226

Woińska S, Godlewska-Żyłkiewicz B (2011) Determination of platinum and palladium in road dust after their separation on immobilized fungus by electrothemal atomic absorption spectrometry. Spectrochim Acta, Part B 66:522–528

Won SW, Mao J, Kwak I-S, Sathishkumar M, Yun Y-S (2010) Platinum recovery from ICP wastewater by a combined method of biosorption and incineration. Bioresour Technol 101:1135–1140

Yong P, Rowson NA, Farr JPG, Harris IR, Macaskie LE (2002a) Bioaccumulation of palladium by *Desulfovibrio desulfuricans*. J Chem Technol Biotechnol 77:593–601

Yong P, Rowson NA, Farr JPG, Harris IR, Macaskie LE (2002b) Bioreduction and biocrystallization of palladium by *Desulfovibrio desulfuricans* NCIMB 8307. Biotechnol Bioeng 80:369–379

Zereini F, Alt F (eds) (2000) Anthropogenic Platinum-group element emissions. Their impact on man and environment. Springer, Berlin

Zereini F, Alt F (eds) (2006) Palladium emission in the environment. Analytical methods, environmental assessment and health effects. Springer, Berlin

Zhou L, Xu J, Liang X, Liu Z (2010) Adsorption of platinum(IV) and palladium(II) from aqueous solution by magnetic cross-linking chitosan nanoparticles modified with ethylenediamine. J Hazard Mat 182:518–524

On the Underestimated Factors Influencing the Accuracy of Determination of Pt and Pd by Electrothermal Atomic Absorption Spectrometry in Road Dust Samples

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Abstract The accurate determination of Pt and Pd in environmental samples requires application of sensitive analytical technique as well as the separation/preconcentration of analytes from complex matrix of such samples. The careful optimization of sample pre-treatment procedure is also essential, but often certain steps of optimization process are neglected. The solid phase extraction procedure based on separation/preconcentration of Pt and Pd on immobilized biomass of fungi *Aspergillus* sp. and determination of analytes by ETAAS was chosen as an example for discussion. The most critical aspects of sample pre-treatment procedure, that affect the accuracy of determination of Pt and Pd in road dust, such as sample storage, sample digestion, transformation of analyte into adequate form, and separation of analytes from interfering matrix are discussed in this chapter. The optimized procedure was applied to the determination of Pt and Pd in road dust collected in Bialystok (Poland). The content of Pt in road dust increased from 93 μg kg^{-1} in 2000 to 263 μg kg^{-1} in 2011, while the content of Pd increased from 43 μg kg^{-1} in 2000 to 328 μg kg^{-1} in 2011.

1 Introduction

The elevated content of Pt and Pd in the urban and roadside environment, which significantly exceeds the geochemical background (1 ng g^{-1}), is mainly connected with emission of these metals from industrial and transport sources. The biological processes occurring in various compartments of environment can lead to the transformation of platinum group elements (PGE) into forms available to plants and

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other living organisms. In the last decade the studies related to emission, occurrence, toxicity, transformation and determination of Pt and Pd in the environment were undertaken (Kalavrouziotis and Koukoulakis 2009; Spada et al. 2012; Zereini et al. 2012). In the near future regular monitoring of these metals in the environment will be probably compulsory.

The determination of Pt and Pd in environmental samples is still a challenging task as a content of these analytes is at a level of ng g^{-1}. The application of sensitive analytical technique, such as inductively coupled plasma mass spectrometry (ICP-MS) (Gomez et al. 2003; Shinotsuka and Suzuki 2007), inductively coupled plasma optical emission spectrometry (ICP-OES) (Herincs et al. 2013), electrothermal atomic absorption spectrometry (ETAAS) (Schuster and Schwarzer 1996; Boch et al. 2002), chemiluminescence (CL) (Malejko et al. 2012) or adsorptive stripping voltammetry (AdVS) (Zimmermann et al. 2003), and careful optimization of sample analytical procedure are necessary to obtain reliable results of analysis. Generally, for elimination of interference arising from complex matrix of samples the application of separation/preconcentration procedure is essential. For this purpose classical methods of separation, such as precipitation and liquid-liquid extraction have been developed. Co-precipitation of Pt with tellurium (Gomez et al. 2003) and Pd with mercury (Zimmermann et al. 2003) was successfully applied for separation of analytes from environmental samples. A variety of dispersive liquid-liquid microextraction (Liang and Zhao 2011) and cloud point microextraction methods (Meeravali et al. 2008) have been used as well. Among other methods, the solid phase extraction (SPE) is most widely recommended (Godlewska-Żyłkiewicz 2004; Myasoedova et al. 2007). The retention mechanism of analytes on solid sorbents include adsorption (Schuster and Schwarzer 1996; Ebrahimzadeh et al. 2010; Rastegarzadeh et al. 2010; Leśniewska et al. 2005; Bagheri et al. 2012), chelation (Rojas et al. 2006, 2009), ion-exchange (Shinotsuka and Suzuki 2007; Nakajima et al. 2009; Krishna et al. 2009; Herincs et al. 2013) and ion-pair formation. Biosorbents, including free and immobilized biomass such as algae *Chlorella vulgaris* (Dziwulska et al. 2004), yeast *Saccharomyces cerevisiae* (Godlewska-Żyłkiewicz and Kozłowska 2005) and fungi *Aspergillus* sp. (Woińska and Godlewska-Żylkiewicz 2011; Malejko et al. 2012), have proved to be an attractive alternative to traditional, commercially available sorbents. The biosorption process has been successfully applied for separation of PGE from environmental samples and their determination by ETAAS.

Even if it is widely recognized that the sample pre-treatment procedure is a main source of errors in the analytical process, certain factors are still underestimated by some analysts. The most critical aspects of the sample pre-treatment procedure, that affect the accuracy of the results, such as sample digestion and separation of analytes from interfering matrix before determination of Pt and Pd in road dust samples by ETAAS technique, will be discussed in detail in this chapter. As an example, the procedure based on separation of Pt and Pd on immobilized biomass of fungi *Aspergillus* sp. (Woińska and Godlewska-Żyłkiewicz 2011), has been chosen.

The analysed samples of road dust were collected from the main intersection located in the centre of Bialystok (Poland) in the period from 2000 to 2011. The fraction of size <0.075 mm was taken for analysis.

2 Digestion Procedure for Road Dust Samples

Inhomogeneous distribution of PGE in road dust and their resistance to various chemicals, complex matrix of such samples often induce problems with complete transfer of the analytes into solution (Balcerzak 2002; Godlewska-Żyłkiewicz 2004). The selected digestion procedure must provide quantitative dissolution of analytes and their transformation into chemical forms suitable for a further pre-treatment step.

Pt and Pd of anthropogenic origin are mainly emitted to the environment in elemental (nano-metallic) and oxide forms (Merget and Rosner 2001). Wet chemical digestions utilizing various mineral acids (HCl, HNO_3, $HClO_4$, HF) in open (Chwastowska et al. 2004) or closed systems heated in convection or microwave ovens are commonly proposed for decomposition of road/tunnel dust or soil (Table 1) (Boch et al. 2002; Limbeck et al. 2003; Matusiewicz and Lesiński 2001; Tsogas et al. 2008). The necessity of using HF for digestion of samples containing silicate matrix was discussed in the literature (Balcerzak 2002; Boch et al. 2002; Leśniewska et al. 2005). According to some authors (Boch et al. 2002; Tsogas et al. 2008) Pd is strongly bound to silicate matrix of dust and ceramic particles emitted to environment from automotive catalysts, therefore its quantitative releasing into solution arises after total digestion of the sample matrix. However, the addition of concentrated HF to the sample induces some analytical problems. The larger amount of dissolved metal ions from silicates or aluminosilicates, e.g. Al(III), Fe(III), Pb(II), Ni(II), Co(II), Cu(II) in the final solution may cause spectral interference in the detection step (Brzezicka and Szmyd 1999; Brzezicka and Baranowska 2001; Godlewska-Żyłkiewicz and Leśniewska 2006, 2010) or problems with efficient separation of matrix.

The removal of these heavy metals from the digested solutions is difficult, because in the presence of HF negatively charged fluoride complexes are formed, which cannot be separated from anionic chlorocomplexes of Pt and Pd, and often are simultaneously enriched on anion-exchange columns (Brzezicka and Baranowska 2001; Godlewska-Żyłkiewicz and Leśniewska 2006). The excess of HF in the analysed solutions might also cause serious damage to the column packing used for the separation of the matrix, e.g. silica gel (Boch et al. 2002). To avoid these adverse effects the evaporation of excess of HF (Limbeck et al. 2003) or masking of fluoride ions with H_3BO_3 (Boch et al. 2002; Tsogas et al. 2008) have been proposed. Some examples of successful application of alone *aqua reqia* for digestion of road dust (Rauch et al. 2000; Müller and Heumann 2000) and BCR 723 (Leśniewska et al. 2005; Godlewska-Żyłkiewicz and Leśniewska 2006; Woińska and Godlewska-Żyłkiewicz 2011) for determination of PGE show that addition of HF to such samples is not essential.

Table 1 Digestion procedures for the determination of Pt and Pd by ETAAS in environmental samples

Sample	Digestion procedure	Evaporation of excess of acids	Separation of analytes	References
Road dust, soil	I step: dry ashing at 400 °C for 1 h; II step: digestion with *aqua regia* in open vessels	Evaporation of acids with 2 mL of HCl (2x); residue was dissolved in 3 mol L^{-1} HCl	Polymethacrylic ester modified with dithizone	Chwastowska et al. (2004)
Urban aerosol	I step: MW digestion with HNO_3 II step: digestion with HF:$HClO_4$ (2:1) in open vessels	Evaporation of acids near to dryness; dilution in 1.2 mol L^{-1} HCl	Silica gel (C18) modified with DEBT	Limbeck et al. (2003)
Tunnel dust	I step: MW digestion with HNO_3:H_2O_2 (5:2); II step: HF addition; III step: H_3BO_3 addition	Dilution in water	Silica gel (C18) modified with DEBT	Boch et al. (2002)
Road dust CW-7	MW digestion with HNO_3: HF:$HClO_3$/ $HClO_4$ (1:1:1)		Electrochemical preconcentration on graphite tube	Matusiewicz and Lesiński (2001)
Road dust BCR-723	I step: MW digestion with HNO_3:HF (2:3) II step: H_3BO_3 addition	Evaporation to dryness; dissolution of residue in 1 mol L^{-1} HNO_3		Tsogas et al. (2008)
Road dust	MW digestion with *aqua regia*	Evaporation near to dryness with 1 mL HCl (2x); dilution in water	Yeast *Saccharomyces cerevisiae* immobilized in calcium alginate	Godlewska-Żyłkiewicz and Kozłowska (2005)
Road dust	MW digestion with *aqua regia*	Evaporation with 2 mL HCl (3x); dilution with water	Fungi immobilized on Cellex-T	Woińska and Godlewska-Żyłkiewicz (2011)

MW—microwave assisted digestion, DEBT—N,N-diethyl-N′-benzoylthiourea

It must be also considered that during storage and pre-treatment of samples, the specific problems connected with chemical reactions and physical processes taking place in solutions or at the phase boundary, e.g. adsorption of analytes on the vessel's surface or changes in the oxidation state may occur. The type of vessels used for preparation and storage of standard and sample solutions (Godlewska-Żyłkiewicz 2002; Cobelo-Garcia et al. 2007), and the roughness of their surface have also an effect on the accuracy of analysis. The memory effect cannot be neglected as well (Kowalska et al. 2005). The storage of Pt solutions in quartz vessels and Pt solutions in glass vessels is recommended, because in this way the adsorption effect is diminished. Efficient cleaning of laboratory ware is possible with solutions containing chemical agents complexing Pt and Pd, such as acidic solutions of thiourea (Godlewska-Żyłkiewicz 2002; Cobelo-Garcia et al. 2007). The crucibles of unknown history should be cleaned before use in concentrated acids, e.g. in a mixture of HCl, HNO_3 and $HClO_4$, HCl or *aqua regia*.

Due to the variety of chemical forms of Pt and Pd in solutions obtained after digestion of samples and various stability of the species, the special treatment of samples should be performed in order to transform the analytes into the form suitable for separation step. A high amounts of chloride and nitrate(V) ions are often added during sample preparation procedure, e.g. during leaching of PGE from road dust with *aqua regia*. It was found that the presence of hydrochloric acid (0.5–4.0 mol L^{-1}) and nitric(V) acid (0.5–2.0 mol L^{-1}) cause increase of the analytical signal of Pt by 20–50 % and the signal of Pd by 30–60 % measured by ETAAS (Godlewska-Żyłkiewicz and Leśniewska 2010). The possibility of formation of stable nitrosyl and/or hydroxynitrate compounds of some PGE (Pt, Ru, Pd) must be carefully considered during sample preparation procedure. The excess of acids should be removed from a digested sample while different species of analytes should be transferred into stable chlorocomplexes. The repeated evaporations of the solution in the presence of concentrated HCl is recommended to that end. It must be stressed that this stage may seriously influence the accuracy of results. On the one hand, the complete evaporation of the solution can lead to the irreversible adsorption of the analyte on the surface of the vessel. On the other hand, often the non-quantitative conversion of analytes takes place as the efficiency of the conversion reaction depends on the number of evaporation steps and the volume of HCl used. Therefore, this step should be optimized experimentally, depending on the type and amount of the digested sample matrix.

In this work the effect of sample pre-treatment step on the accuracy of determination of Pt by ETAAS in road dust was studied in detail. The recovery of Pt from BCR-723 and road dust samples spiked with 20–30 ng of analyte was controlled after variable number of evaporation steps performed with addition of different volumes of concentrated HCl. Such pretreated samples were next loaded on the columns filled with immobilized fungi *Aspergillus* sp. The proper evaporation procedure was chosen on the basis of recovery data and the shape of absorbance signals of the analyte registered from column eluate (Fig. 1). Initially, the digested sample was evaporated two times, almost to dryness, in cleaned quartz crucibles with addition of 1 mL of HCl. However, the repeatability of Pt determination was low (>15 %). Furthermore, a high signal of background was also registered.

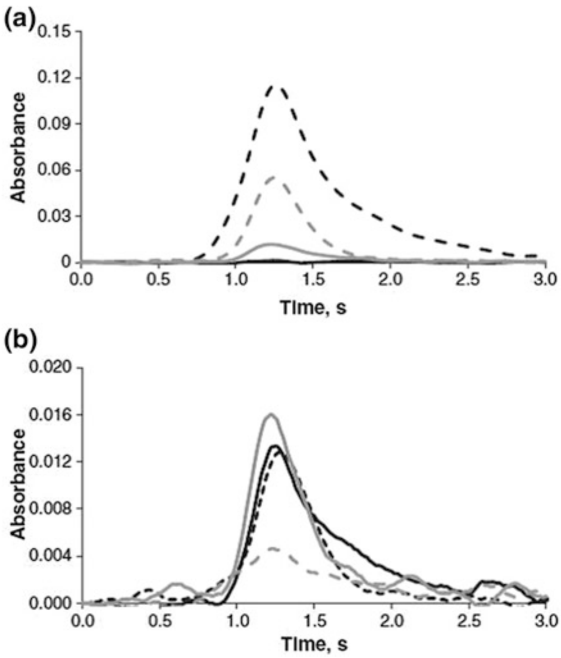

Fig. 1 Atomization signals of Pt from BCR-723 (road dust) (taken from Woińska and Godlewska Żylkiewicz 2011, with Elsevier permission); **a** — Pt in digested sample; --- sample background; Pt in eluent (sample evaporated 2 times with 1 mL HCl); eluent background; **b** — Pt in eluent (sample evaporated 4 x with 1 mL HCl); --- eluent background; Pt in eluent (sample evaporated 3 times with 2 mL HCl); eluent background

When road dust sample was evaporated four times with addition of 1 mL of HCl, the recovery of Pt decreased to 80 %. When samples were evaporated three times with 2 mL of HCl the recovery of Pt from road dust reached 105 %, and from BCR-723 was equal to 107 %. It was confirmed that this procedure provides acceptable recovery of the analyte as well as the efficient elimination of the background signal. For comparison, the atomization signal of Pt obtained from directly injected digested sample is also shown in Fig. 1a.

3 Separation and Determination of PGE

For separation of trace amounts of Pt and Pd from road dust the SPE technique based on biosorption process on various microorganisms was developed (see chap. "Appraisal of Biosorption for Recovery, Separation and Determination of Platinum, Palladium and Rhodium in Environmental Samples"). It was found that fungi *Aspergillus* sp. immobilized on Cellex-T resin were very efficient in terms of selectivity and reproducibility (Woińska and Godlewska-Żyłkiewicz 2011). The analytes were efficiently retained from standard solutions on this biosorbent at pH range from 1 to 4 and quantitatively eluted from the column with thiourea solutions (0.25 mol L^{-1}) prepared in HCl (0.3 mol L^{-1}). However, in order to apply the developed procedure to analysis of road dust samples some further optimization of the procedure had to be done.

Generally, the large content of transition metal ions in the solution obtained after evaporation of digested road dust sample may influence the recovery of the analyte from biosorbent. The retention of the analyte may be diminished due to the competition of the analyte and interfering ions for active sites of sorbent or overloading sorption capacity of the used sorbent. The signals of the analytes registered from eluates are decreased due to interferences from foreign ions co-eluted together with the analytes, and this effect influences their recoveries. Therefore, in many cases the analytical procedure should be completed with additional step of column rinsing before elution of the analyte. The addition of acids, bases and buffering agents used for adjusting of sample pH to the value required to efficient separation as well as reagents used for elution can influence the analytical signal of analytes measured by ETAAS.

The retention of palladium and platinum on the fungi *Aspergillus* sp. immobilized on Cellex-T was not diminished in the presence of high excess of transition metal ions (10 mg L^{-1}-10 g L^{-1} of Al(III), Cr(III), Co(II), Fe(III), Ni(II), and Pb(II)) (Woińska and Godlewska-Żyłkiewicz 2011). However, their presence considerably influenced the recovery of analytes. The strongest decrease of platinum and palladium recoveries (to 46.5 and 56.2 %, respectively) was observed in the presence of Co(II) ions (10 mg L^{-1}). The significant background signals registered from eluate solutions indicate that transition metal ions nonspecifically retained on the low mass of sorbent were co-eluted together with the analytes. Removing of matrix ions retained on the sorbent was performed by rinsing the column before the elution step with water or nitric acid of different concentrations. The example below shows the process of optimization of rinsing procedure, which had been used for the elimination of negative effect of Co(II) ions (10 mg L^{-1}) on the recovery of Pt (50 μg L^{-1}) from the column (Fig. 2). As mentioned above the recovery of Pt from such solution was only 46.5 %. Rinsing the column with 3, 5 or 20 mL of water resulted in significant reduction of the background signal and increase of Pt recovery to 55, 64 and 78 %, respectively (Fig. 2a). Because the recovery of Pt was not quantitative, solutions of nitric acid of various concentrations (0.001–0.1 mol L^{-1}) were tested for removal of Co(II) ions from the column. As can be seen in Fig. 2b, the use of 3 and 5 mL of 0.001 mol L^{-1} HNO_3 resulted in 51 and 83 % recovery of Pt. The recovery equals 79 % was obtained using for this purpose of 3 mL of 0.05 mol L^{-1} HNO_3. Accurate results of the analysis (recovery: 93.2 ± 2.0 %, n = 3) and the total elimination of the background signal was obtained when column was rinsed with 5 mL of 0.05 mol L^{-1} HNO_3. The small losses of Pt (recovery: 86 %) with rinsing solution were observed when higher concentration of nitric acid (>0.1 mol L^{-1}) was used. The effectiveness of the developed procedure was proved by analysis of standard Pt solutions (50 μg L^{-1}) containing a high concentrations of foreign ions, namely a mixture of Al(III), Cr(III) and Co(II) ions of total concentration from 30 mg L^{-1} to 2,608 mg L^{-1}. The recovery of Pt from such solutions was in the range from 101.7 ± 2.3 % to 106.8 ± 5.2 % (n = 4). The recovery of platinum decreased to 60.3 ± 0.4 % (n = 3), when the solution contained as much as 10 g L^{-1} of Al(III), 400 mg L^{-1} of Cr(III) and 30 mg L^{-1} of Co(II). In the same way the procedure of column rinsing was optimized for Pd determination. The recovery of Pd (50 μg L^{-1}) from the column in the presence of other

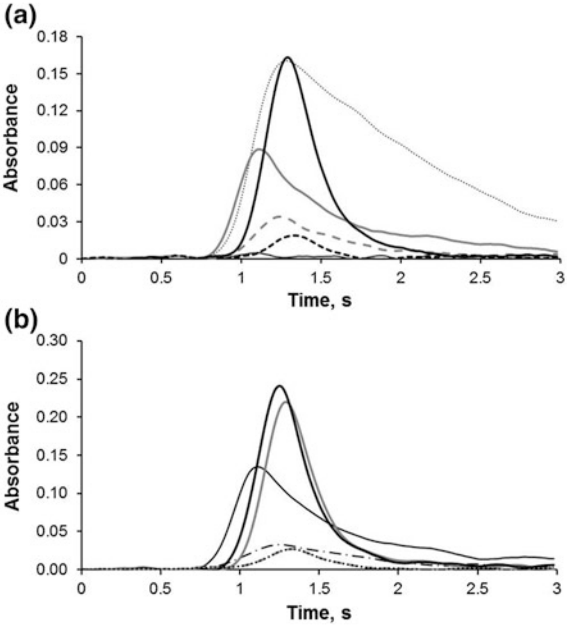

Fig. 2 Atomization signals of Pt from solutions containing 50 μg L^{-1} Pt + 10 mg L^{-1} Co after separation on fungi *Aspergillus* sp immobilized on Cellex-T: **a** —— Pt signal in sample solution; ······ sample background; Pt signal in eluent, column rinsed with: —— 3 mL of H_2O, —— 20 mL of H_2O; eluent background, column rinsed with: - - - 3 mL of H_2O, - - - 20 mL of H_2O; **b** Pt signal in eluent, column rinsed with: —— 3 mL 0.001 mol L^{-1} HNO_3, —— 5 mL 0.001 mol L^{-1} HNO_3, —— 5 mL 0.05 mol L^{-1} HNO_3; eluent background, column rinsed with: - - - 3 mL 0.001 mol L^{-1} HNO_3, - - - - 5 mL 0.001 mol L^{-1} HNO_3, ········ 5 mL 0.05 mol L^{-1} HNO_3

ions (2.5 g L^{-1} of Fe(III), 500 mg L^{-1} of Ni(II), 9 mg L^{-1} of Co(II) and 6 mg L^{-1} of Pb(II)) amounted to 100.3 ± 0.4 % (n = 4). Finally, it was found that using of 5 mL of 0.05 mol L^{-1} HNO_3 for column rinsing in case of Pt determination, or 5 mL of 0.1 mol L^{-1} HNO_3 in the case of Pd determination, allows for quantitative recovery of analytes and significant elimination of interferences even in the presence of 50,000–60,000-fold excess of other ions.

4 Analysis of Road Dust Samples

The content of Pt and Pd in road dust samples collected in the center of Białystok (300,000 inhabitants, main intersection of urban roads, sampling at the distance of 2 meters from a footpath with traffic lights) was determined using a developed procedure consisting of digestion of samples in *aqua regia*, evaporation of samples with concentrated HCl, separation of analytes on fungi *Aspergillus* sp. immobilized on Cellex-T and their determination by ETAAS. The obtained results are presented in

Fig. 3 Pt and Pd content in road dust collected in years 2000-2011 from main intersection in Bialystok

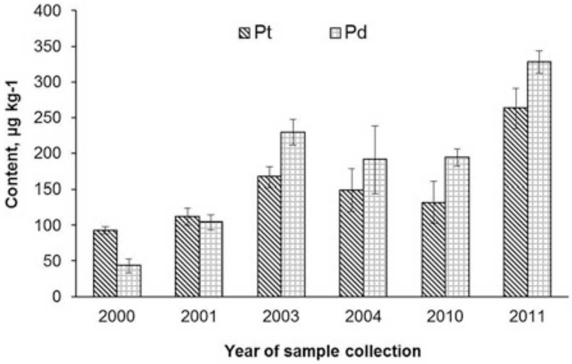

Fig. 3. The content of Pt in road dust increased from 93 µg kg^{-1} in 2000 to 263 µg kg^{-1} in 2011, while the content of Pd increased from 43 µg kg^{-1} in 2000 to 328 µg kg^{-1} in 2011. These values are significantly higher than background values, which suggest the input of PGE to the environment from automobile catalyst systems. The rapid increase of content of PGE in road dust is probably an effect of 140 % increasing of the number of cars registered in Białystok within this period (according to the Department of Inhabitants Service, City Office, Białystok from 58,000 in 2001 to 138,407 in 2011). The increase of Pd content in road dust was more rapid than the increase of Pt, which can be related to the changes in composition of catalytic converters introduced at the beginning of 2000, when Pt was replaced by Pd due to its high price. Since 2003 almost constant ratio of content of Pt to Pd in collected road dust has been observed ($Pt_{content}/Pd_{content}$. = 0.746 ± 0.055).

The obtained values of Pt and Pd content in road dust in Białystok are similar to the results obtained in the UK (Prichard et al. 2009), Spain (Simitchiev et al. 2008), the USA (Spada et al. 2012) or Greece (Tsogas et al. 2008) (Fig. 4) in road dust collected from the places with high traffic. The traffic intensity, the speed of cars and driving conditions influence the emission rate of PGE. The emission is also higher during continued stop/start cycles as well as during engine's ignition (Tsogas et al. 2008), what often happens at traffic lights. The content of PGE in samples collected in Białystok is quite high, which can be explained by the sampling place situated close to traffic lights. The content of Pt and Pd in samples collected in 2009 from ring road of the city was much lower, namely 48 and 97 µg kg^{-1}. The content of PGE in tunnel dust (the USA) is among highest values.

The PGE content in road dust obtained in Hong Kong and Macao (China) is also comparable to our results, as in those cities catalytic converters were applied to vehicles as early as in European countries (Pan et al. 2013). In Beijing and Shanghai (China) the PGE content in road dust samples is relatively lower, what was explained by considerable dilution of dust due to engineering (road) construction in the sampling time of 2007. The lower content of PGE in road dust in Kolkata (India), Qingdao and Wuhan (China), and Seoul (Korea) (Lee et al. 2012) can be connected with shorter time period when vehicles have been equipped with catalytic converters.

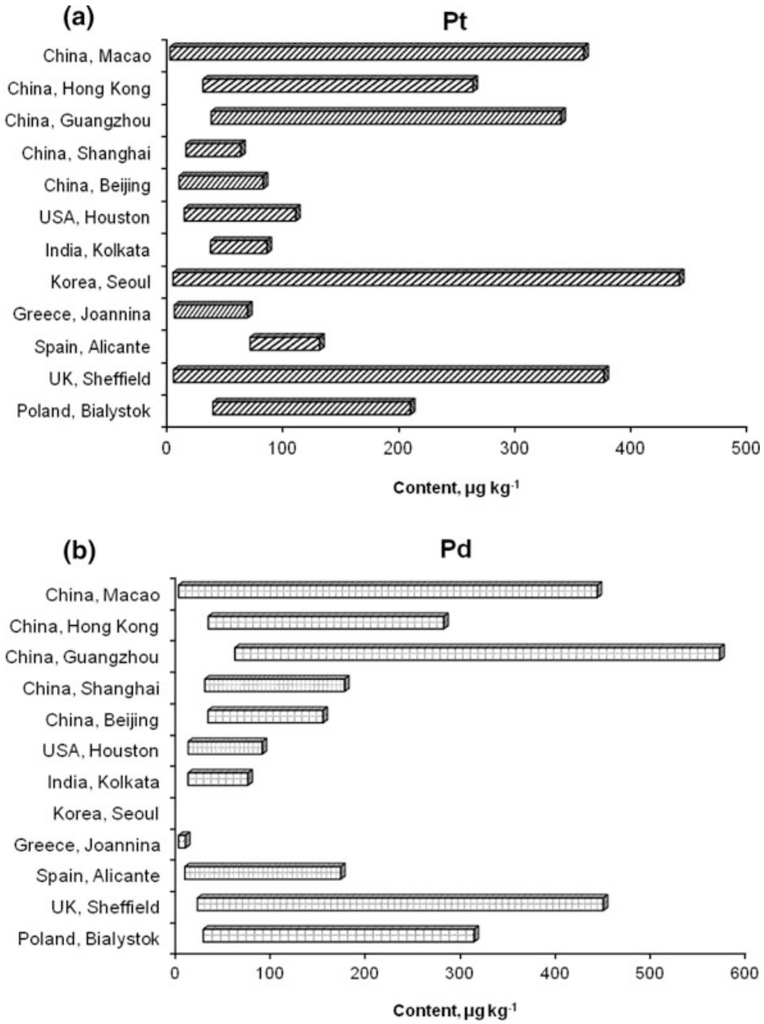

Fig. 4 Ranges of Pt (a) and Pd (b) content in road dust in different countries (Pan et al. 2013; Spada et al. 2012; Lee et al. 2012; Tsogas et al. 2008; Smitchiev et al. 2008; Prichard et al. 2009, this work)

5 Conclusions

It is of key importance that the reliable determination of Pt and Pd in road dust by spectrometric techniques (e.g. ETAAS) requires careful optimization of sample pretreatment procedure. The steps, which seems to be less important, as evaporation of acids from digested samples or rinsing of column after separation of analytes, have the significant effect on the final result, what was described in this chapter. Therefore, all steps of procedure should be optimized experimentally using samples of similar matrices or certified reference materials.

References

Bagheri A, Taghizadeh M, Behbahani M, Asgharinezhad AA, Salarian M, Dehghani A, Ebrahimzadeh H, Amini MM (2012) Synthesis and characterization of magnetic metal-organic framework (MOF) as a novel sorbent, and its optimization by experimental design methodology for determination of palladium in environmental samples. Talanta 99:132–139

Balcerzak M (2002) Sample digestion methods for the determination of trace of precious metals by spectrometric techniques. Anal Sci 18:737–750

Boch K, Schuster M, Risse G, Schwarzer M (2002) Microwave-assisted digestion procedure for the determination of palladium in road dust. Anal Chim Acta 459:257–265

Brzezicka M, Baranowska I (2001) Methods for separation of trace amounts of platinum and investigation of the influence of interfering elements during platinum determination in copper ores and copper concentrates by graphite furnace atomic absorption spectrometry. Spectrochim Acta 56B:2513–2520

Brzezicka M, Szmyd E (1999) Investigation of the influence of interfering elements on the determination of palladium in copper ores by graphite furnace atomic absorption spectrometry. Spectrochim Acta 54B:883–889

Chwastowska J, Skwara W, Sterlińska E, Pszonicki L (2004) Determination of platinum and palladium in environmental samples by graphite furnace atomic absorption spectrometry after separation on dithizone sorbent. Talanta 64:224–229

Cobelo-Garcia A, Turner A, Millward GE, Couceiro F (2007) Behaviour of palladium(II), platinum(IV), and rhodium(III) in artificial and natural waters: influence of reactor surface and geochemistry on metal recovery. Anal Chim Acta 585:202–210

Dziwulska U, Bajguz A, Godlewska-Żyłkiewicz B (2004) The use of algae C*hlorella vulgaris* immobilized on Cellex-T support for separation/preconcentration of trace amounts of platinum and palladium before GFAAS determination. Anal Lett 37:2189–2203

Ebrahimzadeh H, Tavassoli N, Amini MM, Fazaeli Y, Abedi H (2010) Determination of very low levels of gold and palladium in wastewater and soil samples by atomic absorption after preconcentration on modified MCM-48 and MCM-41 silica. Talanta 81:1183–1188

Godlewska-Żyłkiewicz (2002) Hazards of error in the palladium storage and determination by GFAAS. Anal Bioanal Chem 372:593–596

Godlewska-Żyłkiewicz B (2004) Preconcentration and separation procedures for the spectrochemical determination of platinum and palladium. Microchim Acta 147:189–210

Godlewska-Żyłkiewicz B, Kozłowska M (2005) Solid phase extraction using immobilized yeast *Saccharomyces cerevisiae* for determination of palladium in road dust. Anal Chim Acta 539:61–67

Godlewska-Żyłkiewicz B, Leśniewska B (2006) Sources of error and their elimination for spectrometric determination of palladium in environmental samples. In: Zereini F, Alt F (eds) Palladium emission in the environment. Springer, Berlin Heidelberg, pp 97–109

Godlewska-Żyłkiewicz B, Leśniewska B (2010) Analysis of road dust: determination of platinum and palladium by GFAAS and ICP MS techniques. In: Żyrnicki W, Borkowska-Burnecka J, Bulska E, Szmyd E (eds) Methods of analytical atomic spectrometry. Theory and practice. Malamut, Warsaw, pp 375–384 (in Polish)

Gomez MB, Gomez MM, Palacios MA (2003) ICP-MS determination of Pt, Pd and Rh in airborne and road dust after tellurium coprecipitation. J Anal At Spectrom 18:80–83

Herincs E, Puschenreiter M, Wenzel W, Limbeck A (2013) A novel flow-injection method for simultaneous measurement of platinum (Pt), palladium (Pd) and rhodium (Rh) in aqueous soil extracts of contaminated soil by ICP-OES. J Anal Atom Spectrom 28:354–363

Kalavrouziotis IK, Koukoulakis PH (2009) The environmental impact of the platinum group elements (Pt, Pd, Rh) emitted by the automobile catalyst converters. Water Air Soil Pollut 196:393–402

Kowalska J, Asztemborska M, Godlewska-Żyłkiewicz B, Golimowski J (2005) Systematic errors in the determination of trace metals, Part II. Memory effects of quartz vessels used for samples preparation in the determination of ultra-trace levels of platinum. Microchim Acta 150:55–58

Krishna MVB, Ranjit M, Chandrasekaran K, Karunasagar D (2009) On-line preconcentration and recovery of palladium from waters using polyaniline (PANI) loaded in mini-column and determination by ICP-MS; elimination of spectral interferences. Talanta 79:1454–1463

Lee HY, Chon HT, Sager M, Marton L (2012) Platinum pollution in road dusts, roadside soils, and tree barks in Seoul, Korea. Environ Geochem Health 34:5–12

Leśniewska B, Godlewska-Żyłkiewicz B, Hulanicki A (2005) The effect of hydrofluoric acid on determination of platinum and palladium in road dust applying inductively coupled plasma mass spectrometry. Anal Chem (Warsaw) 50:945–950

Liang P, Zhao E (2011) Determination of trace palladium in complicated matrices by displacement dispersive liquid-liquid microextraction and graphite furnace atomic absorption spectrometry. Microchim Acta 174:153–158

Limbeck A, Rendl J, Puxbaum H (2003) ETAAS determination of palladium in environmental samples with on-line preconcentration and matrix separation. J Anal At Spectrom 18:161–165

Malejko J, Szygałowicz M, Godlewska-Żyłkiewicz B, Kojło A (2012) Sorption of platinum on immobilized microorganisms for its on-line preconcentration and chemiluminescent determination in water samples. Microchim Acta 176:429–435

Matusiewicz H, Lesiński M (2001) Electrodeposition sample introduction for ultra trace determinations of platinum group elements (Pt, Pd, Rh, Ru) in road dust by electrothermal atomic absorption spectrometry. Int J Environ Anal Chem 82:207–223

Merget R, Rosner G (2001) Evaluation of the health risk of platinum group metals emitted from automotive catalytic converters. Sci Total Environ 270:165–173

Meeravali NN, Kumar SJ, Jiang SJ (2008) Interference free ultra trace determination of Pt, Pd and Au in geological and environmental samples by inductively coupled plasma quadrupole mass spectrometry after a cloud point extraction. J Anal At Spectrom 23:854–860

Müller M, Heumann KG (2000) Isotope dilution inductively coupled plasma quadrupole mass spectrometry in connection with a chromatographic separation for ultra trace determinations of platinum group elements (Pt, Pd, Ru, Ir) in environmental samples. Fresenius J Anal Chem 368:109–115

Myasoedova GV, Mokhodoeva OB, Kubrakova IV (2007) Trends in sorption preconcentration combined with noble metal determination. Anal Sci 23:1031–1039

Nakajima J, Ohno M, Chikama K, Seki T, Oguma K (2009) Determination of trace of palladium in stream sediment and auto catalyst by FI-ICP-OES using on-line separation and preconcentration with QuadraSil TA. Talanta 79:1050–1054

Pan S, Sun Y, Zhang G, Chakraborty P (2013) Spatial distributions and characteristics of platinum group elements (PGEs) in urban dusts from China and India. J Geochem Explor 128:153–157

Prichard HM, Sampson J, Jackson M (2009) A further discussion of the factors controlling the distribution of Pt, Pd, Rh and Au in road dust, gullies, road sweeper and gully flusher sediment in the city of Sheffield, UK. Sci Total Environ 407:1715–1725

Rastegarzadeh S, Pourreza N, Kiasat AR, Yahyavi H (2010) Selective solid phase extraction of palladium by adsorption of its 5(p-dimethylaminobenzylidene)rhodanine complex on silica-PEG as a new adsorbent. Microchim Acta 170:135–140

Rauch S, Motelica-Heino M, Morrison GM, Donard OFX (2000) Critical assessment of platinum element determination in road and urban river sediments using ultrasonic nebulisation and high resolution ICP-MS. J Anal At Spectrom 15:329–334

Rojas FS, Ojeda CB, Pavón JMC (2006) Automated on-line separation preconcentration system for palladium determination by graphite furnace atomic absorption spectrometry and its application to palladium determination in environmental and food samples. Talanta 70:979–983

Rojas FS, Ojeda CB, Pavón JMC (2009) Simultaneous determination of palladium and rhodium using on-line column enrichment and electrothermal atomic absorption spectrometric detection. J Anal Chem 64:241–246

Schuster M, Schwarzer M (1996) Selective determination of palladium by on-line column preconcentration and graphite furnace atomic absorption spectrometry. Anal Chim Acta 328:1–11

Shinotsuka K, Suzuki K (2007) Simultaneous determination of platinum group elements and rhenium in rock samples using isotope dilution inductively coupled plasma mass spectrometry after cation exchange separation followed by solvent extraction. Anal Chim Acta 603:129–139

Simitchiev K, Stefanova V, Kmetov V, Andreev G, Sanchez A, Canals A (2008) Investigation of ICP-MS spectral interferences in the determination of Rh, Pd and Pt in road dust: assessment of correction algorithms via uncertainty budget analysis and interference alleviation by preliminary acid leaching. Talanta 77:889–896

Spada N, Bozlaker A, Chellam S (2012) Multi-elemental characterization of tunnel and road dusts in Houston, Texas using dynamic reaction cell-quadrupole inductively coupled plasma-mass spectrometry: evidence for the release of platinum group and anthropogenic metals from motor vehicles. Anal Chim Acta 735:1–8

Tsogas GZ, Giokas DL, Vlessidis AG, Evmiridis NP (2008) On the re-assessment of the optimum conditions for the determination of platinum, palladium and rhodium in environmental samples by electrothermal atomic absorption spectrometry and microwave digestion. Talanta 76:635–641

Woińska S, Godlewska-Żyłkiewicz B (2011) Determination of platinum and palladium in road dust after their separation on immobilized fungus by electrothermal atomic absorption spectrometry. Spectrochim Acta, Part B 66:522–528

Zereini F, Alsenz H, Wiseman CLS, Püttmann W, Reimer E, Schleyer R, Bieber E, Wallasch M (2012) Platinum group elements (Pt, Pd, Rh) in airborne particulate matter in rural versus urban areas of Germany: Concentrations and spatial patterns of distribution. Sci Total Environ 416:261–268

Zimmermann S, Messerschmidt J, van Bohlen A, Sures B (2003) Determination of Pt, Pd and Rh in biological samples by electrothermal atomic absorption spectrometry as compared with adsorptive cathodic stripping voltammetry and total reflection X-ray fluorescence analysis. Anal Chim Acta 498:93–104

Application of Solid Sorbents for Enrichment and Separation of Platinum Metal Ions

Krystyna Pyrzynska

Abstract Determination of platinum metal ions in environmental samples requires very often pre concentration and separation due to the low content of these metals and the high concentration of interfering matrix components. Solid phase extraction technique with different kind of solid sorbents offers for this purpose high enrichment factor, rapid phase separation and the ability of combination with different detection techniques in the form of *on*-line and *off*-line mode. The recent developments in this area published over the last 5 years will be presented and discussed.

1 Introduction

Platinum group elements (PGEs) can be naturally found only at very low concentration in the earth crust. However, their increasing use in vehicle exhaust catalysts, in addition to some other applications such industry, jewellery, anticancer drugs, cause their anthropogenic emission and spread in the environment.

The determination of PGEs in environmental samples is difficult due to high concentration of interfering matrix components and the low content of the analytes in most samples. In order to solve these problems conventional separation techniques have been often exploited. Among different separation and pre concentration techniques, batch and column approaches in which PGEs are sorbed on different water-insoluble solid materials and further eluted with acids or complexing reagents have been widely used. Solid phase extraction (SPE) offers a number of important advantages in comparison with classical liquid-liquid extraction, such as reduced organic solvents usage and exposure, high enrichment factor, rapid phase separation and the ability of combination with different detection techniques (Das et al. 2012; Augusto et al. 2013). Moreover, it can be easily implemented and controlled in flow

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systems to perform appropriate sample pretreatment. Column sorption is mainly applied to enhance the sensitivity of flame atomic absorption spectrometry (FAAS) and inductively coupled plasma atomic emission spectrometry (ICP OES) determinations as well as to separate the analytes from potentially interfering matrix components, particularly for electrothermal AAS and ICP mass spectrometry detection.

The mechanism of sorption depends on the nature of a given sorbent and may include simple adsorption, complexation or ion-exchange. Adsorption occurs through van der Waals forces or hydrophobic interactions, which occurs when the solid sorbent is highly nonpolar. The most common materials of this type include octadecyl silica and styrene-divinylbenzene copolymers that provide additional π–π interactions when PGEs are complexed with ligands containing π-electrons. The presence of appropriate functional groups in solid matrices is needed for ion-exchange or chelation. Binding of the analytes to these groups is dependent on their nature as well as the buffering conditions. The choice of solid material for enrichment and removal of PGEs should be based on the content of the analyte, sample matrix and technique for final detection, whereas higher enrichment factors can be obtained under adequate experimental conditions (time of loading sample, sorbent mass, volume of eluent).

The purpose of this paper is to present and discuss some of the recent tendencies on the research related to novel sorbent materials for the separation and pre concentration of platinum metal ions from environmental and geological samples. There is a growing interest in sorbents based on nano structured materials such as magnetic nanoparticles and carbon nanotubes. Ion imprinted polymers properties are remarkable because of their high selectivity towards the target ion due to a memory effect resulting from their preparation process. Several biological materials containing a variety of functional sites have received increasing attention and their analytical performance for enrichment of PGEs is presented in the separate chapter. In the following sections the applications of these new sorbents proposed over the last 5 years are discussed in more details. Earlier developments have been presented in the reviews (Godlewska-Żyłkiewicz 2004; Myasoedova et al. 2007; Hubicki et al. 2008; Balcerzak 2011; Mladenova et al. 2012).

2 Nanoparticles

The field of nanometer-sized materials has gained the attention in recent years due to their special properties (Lucena et al. 2011; Pyrzynska 2013). Nanoparticles are cluster of atoms or molecules of metal oxide, ranging in size from 1 nm to almost 100 nm. One of their interesting properties is that a high percentage of the atoms of the nanoparticles is on the surface and they can bind other atoms that possess strong chemical activity. Inorganic nanoparticles such as Al_2O_3, Fe_3O_4, TiO_2, SiO_2, ZrO_2 and CeO_2 exhibit large specific surface area, high sorption capacity and high chemical activity, so they are promising solid phase extractants. Their sorption properties depend on morphology, crystal structure, specific surface area, hydroxyl coverage and surface impurities. The modification of the sorbent surface with organic compounds, especially chelating ones, increases their selectivity. The modification is generally made by chemical bonding of the chelating ligand on nanometer oxide or by the impregnating the solid matrix with appropriate specific organic molecule. Physical binding is the most simple to use in practice, but chemical bonding allows elevated lifetime for modification due to covalent bonds between ligand and the support. This property avoids the possible loss of the reagent from the sorbent surface during sample loading process or elution steps.

The sorption of Pd(II), Rh(III) and Pt(IV) from diluted acid solution onto Fe_3O_4 nanoparticles was investigated by Uheida et al. (2006). The maximum loading capacities for these metal ions were 3.72, 15.3 and 13.27 mg g^{-1}, respectively. It was found that 0.5 mol L^{-1} HNO_3 could eluted all of the metal ions simultaneously, while 1 mol L^{-1} $NaHSO_3$ was an effective eluting solution for Rh(III) and 0.5 mol L^{-1} $NaClO_4$ for Pt(IV). In competitive sorption, the nanoparticles showed stronger affinity for Rh(III) than for palladium and platinum ions. Halloysite nanotubes (layered aluminosilicate clay mineral) functionalized by murexide have been proposed as a highly selective sorbent for pre concentration and separation of Pd(II) (Li et al. 2012). The maximum sorption capacity at pH 1 was found to be 42.86 mg g^{-1}. An enrichment factor of 120 was accomplished. Rh(III) complexed with 2,3,5,6, -tetra(2-pirydyl) pyrazine at pH 4.1 was preconcentrated on the organo-nano clay and then eluted with 3 mol L^{-1} HCl solution (Afzali et al. 2010).

The alternative use of nanomaterials in sample preparation protocols is to immobilize them onto a solid support, particularly with magnetic properties, such as magnetite (Fe_3O_4) and/or maghemite (γ-Fe_2O_3) (Lopez-Lorento et al. 2011; Chen et al. 2011). These hybrid nano materials can be easily separated from the dispersion with the aid of an external magnetic field. Schematic description of solid phase extraction procedure using magnetic nanoparticles are presented in Fig. 1. Additionally, the protecting coating of nano materials stabilizes the magnetic shell and can also be used for further functionalization to obtain multifunctional magnetic nano materials. The potential of non-modified magnetic Fe_3O_4 nanoparticles for determination of trace amounts of Pd(II) and Rh(III) ions in Pd-Ir alloy and road dust by FAAS after simultaneous enrichment and separation at pH 10–12 has been evaluated (Mohammadi et al. 2011). No filtration or centrifugation was necessary. With respect to eluent volume (2 mL of 1 mol L^{-1} HCl), a 150 pre concentration factor was obtained.

Several modifications were used to immobilize different compounds on the surface of magnetic nanoparticles to increase their selectivity. For palladium pre concentration pyridine (Bagheri et al. 2012) and for simultaneous enrichment of palladium and platinum (Zhou et al. 2010) ethylenediamine were used. For trace noble metals (Ru, Rh, Pd, Pt, Ir and Au) mercapto groups have been proposed (Li et al. 2011a). The last sorbent was immobilized on the inner walls of a knotted reactor in the flow injection on-line displacement solid phase extraction method. The procedure began with the presorption of Cu(II) via complexing with the thiol group in the sorbent and followed by subsequent on-line displacement of copper

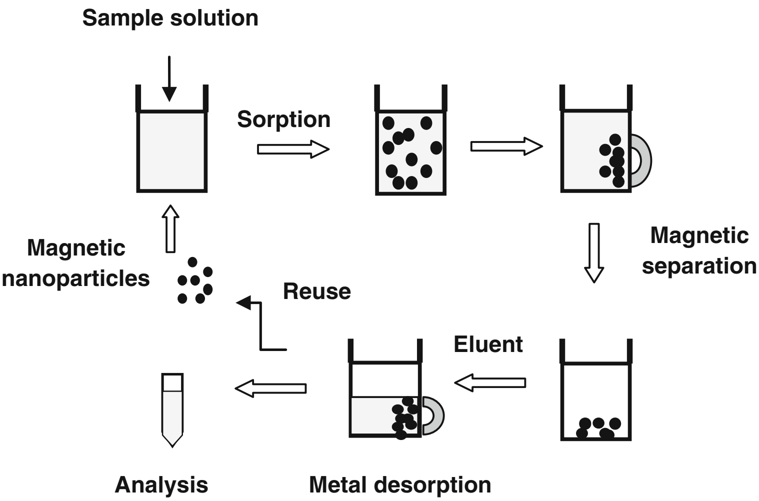

Fig. 1 Schematic description of solid phase extraction procedure using magnetic nanoparticles

ions by noble metals owing to their stronger affinity to the functionalized sorbent relative to Cu(II). Such displacement reaction could not occur with heavy metal ions (such as Co(II), Mn(II), Ni(II), Cr(III), Pb(II), Cd(II), Fe(III) and Zn(II)) with weaker affinity to the thiol groups. Thus, the possible interferences from these metal ions were eliminated or minimized and the proposed procedure could tolerate their presence at the concentration four orders of magnitude of those of noble metals.

A new mode of dispersive solid phase extraction based on ferrofluid (silica-coated magnetic nanoparticles) have been developed and applied for separation of palladium in natural waters and road dust (Farahani et al. 2013). Briefly, 15 mg of magnetic nanoparticles were injected rapidly into 50 mL of sample solution (containing Pd(II), sodium diethyldithiocarbamate for complexation of analyte and phosphate buffer at pH 6) through a syringe. Nanoparticles were separated from the dispersion with the aid of magnet and supernatant was discarded simply by decanting it. Then 0.75 mL of acetylacetone was introduced to desorb Pd(II) complex by sonication. Finally, the mixture was exposed again to the magnet and the clear solution containing the eluted metal ions was transferred to the glass tube and determined by FAAS with detection limit of 0.35 μg L^{-1}. Sorption capacity of the proposed ferrofluid for Pd(II) was 24.6 mg g^{-1}.

3 Carbon-Based Sorbents

Among carbon-based sorbents, activated carbon was certainly one of the first materials applied in SPE and it has been widely used in water and wastewater treatment. It has received great interest due to its large surface area, high sorption capacity, porous structure and low cost. The surface structure of activated carbon is highly complex and depends on the raw material used for producing it and on the method of production as well as on the pretreatment process. Pretreatment by oxidant acids causes reorganization of its porous structure and could also affect the capacity towards the metal ions (Yin et al. 2007). The sorption of ionic species is mainly controlled by electrostatic forces, which are related to the various surface functional groups. The nature and concentration of these groups may be modified by suitable thermal or chemical treatment. The most common oxygen functional groups on the surface of carbon materials are carboxyl, carbonyl, hydroxyl, phenol, quinine and lactone. Nitrogen containing groups could be introduced after ammonia treatment at high temperature (Jia et al. 2002).

Several authors have clearly proved that the sorption of platinum and palladium ions as well as gold in acidic solution can be accompanied by the deposition of metal clusters onto a surface of carbon material (Choi et al. 2002; Simanova et al. 2008; Dobrowolski et al. 2008; Bystrzejewski and Pyrzynska 2013). This is a different mechanism in comparison to sorption of organic molecules (which requires high porosity) and heavy metals ions (which is enabled via the electrostatic attractions between the negatively charged surface of carbon material and metal cations). PGEs have sufficiently high redox potentials and oxidize the surface of a carbon sorbent. Due to the redox reactions occurring during retention of PGEs on activated carbon, their desorption is a critical step in the analytical procedures (Dobrowolski et al. 2008; Kononova et al. 2010).

Recent research has focused on modification of activated carbon surface for creation of specific functional groups to enhance removal of PGE ions. The new sorbents prepared by immobilization of thiouracil (Vassileva et al. 2008), 2, 6-diaminopyridine (Li et al. 2011b) and ethyl-3-(2-aminoethylamino)-2-chlorobut-2-enoate (To et al. 2011) on activated carbon have been proposed. The adsorption capacity for Pd(II) and Pt(IV) was the highest in the case of modification with that last ligand (92 and 126 mg g^{-1}, respectively). Acidic solution of thiourea was used for elution of adsorbed metal ions. Activated carbon modified with 2,6-diaminopyridine could be used for selective separation of platinum, palladium and gold ions from other PGEs in acidic solution (Li et al. 2011b). At pH 1, Pt(IV), Pd(II) and Au (III) were quantitatively sorbed simultaneously, while the recovery of Ir(III), Rh(III) and Ru(IV) were only 13, 1.6 and 8 %, respectively, under these conditions (Fig. 2).

Carbon nanotubes (CNTs), the newer generation of carbon sorbents, have also great analytical potential as a solid phase extraction sorbent (Ravelo-Perez et al. 2010; Pyrzynska 2010; Perez-Lopez and Marcoçi 2012; Zhang et al. 2013). The characteristic structures and electronic properties of CNTs allow them to interact via non-covalent forces, such as hydrophobic interactions, hydrogen bonding, π–π stacking, electrostatic and van der Waals forces. Multi-walled CNTs are preferred over single-walled ones as the presence of concentric grapheme sheets resulted in an enhanced interaction with the analytes (El-Sheikh et al. 2012).

Glaseminezhad et al. (2009) have proposed the application of the oxidized CNTs for pre concentration and separation of Rh(III), which was previously complexed with 1-(2-pyridulazo)-2-naphtol. The adsorbed complex was then eluted using

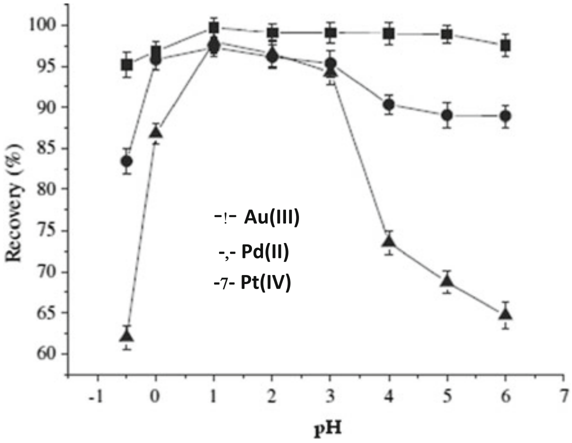

Fig. 2 Effect of pH on sorption; of (■) Au (III), (●) Pd (II) and (▲) Pt (IV) on activated carbon modified with 2,6,-diaminopyridine. Metal concentration 10 mg/L; amount of sorbent 30 mg, contact time 30 min (Li et al. 2011b). Reproduced with permission from Springer

N–*N*-dimethylformamide and pre concentration factor was 120. The sorption capacity for rhodium ions was 6.6 mg g^{-1}. Oxidized CNTs modified with 5-(4′ -dimethylaminobenzyliden)-rhodamine have been proposed for pre concentration of trace level of palladium (Afzali et al. 2012). The proposed method permitted a large pre concentration factor (about 200), low detection limit (0.3 μg L^{-1}) with FAAS detection and sorption capacity of 2.34 mg g^{-1}. Higher sorption capacity for palladium (15.7 mg g^{-1}) have been reported for oxidized CNTs without chelating agent at pH 6 (Yuan et al. 2011). Elution was done with 3 mol L^{-1} HNO_3 achieving the limit of detection of 0.3 μg L^{-1} (FAAS detection). The possibility of Pd(II) reduction on the surface of CNTs was not reported. The methods were applied to the determination of palladium in water, fly ash and road dust samples. Recently, very high sorption capacity (101.5 mg g^{-1}) for Pd(II) on CNTs modified with poly (*N*-phenylethanoloamine) has been achieved (Behbahani et al. 2013). The vast majority of transition metal ions that exist in natural samples have no interferences with the determination of palladium. However, the effect of other platinum metal ions was not checked. The proposed procedure with detection limit of 0.09 μg L^{-1} (FAAS detection) was applied for determination of Pd(II) in spiked natural water and soil samples.

4 Ion Imprinted Polymers

Ion imprinted polymers (IIPs), possessing tailor-made recognition sites, can specifically rebind to a target ion in preference to analogous compounds or ions. The general procedure for IIPs elaboration consists in the preparation of ligand-metal complex and its copolymerization with a cross-linker in order to create three dimensional recognition cavities inside the polymer network. The resultant imprints possess a steric and chemical memory for the template. Its selectivity is based on the specificity of the ligand, the coordination geometry and coordination number of the ions as well as their charge and sizes. This selectivity is particularly important when analyzing complex matrices.

As organic imprinted polymers are mainly prepared by free radical polymerization, vinyl groups are the classic type of polymerizable functions suiting for this purpose. The used ligands act as bi-functional reagents: one functionality comes from their chelating ability and the other one from their vinyl function. Another method for preparation of IIPs is trapping of non-functionalized ligand inside the polymer network. These different ways for incorporating the ligands have been presented in details in the recent reviews (Hu et al. 2013; Branger et al. 2013). Whatever ligand is chosen to be introduced, the interactions between the polymer framework and the complexed ion are based on coordinative bonds from some electron donating heteroatoms (such as oxygen, nitrogen or sulfur) to the unfilled orbitals of the outer sphere of the metal ions.

Daniel et al. (2005) evaluated different quinoline derivatives, e.g. 8-aminoquinoline (AQ), 8-hydroxyquinoline (HQ) and 8-mercaptoquinoline (MQ) as one of the ligands during the synthesis of IIPs employing ternary mixed ligand complex with Pd(II) in the presence of 4-vinyl pyridine. The affinity distribution curves indicated that rebinding took place via covalent mode in the case of AQ- and HQ-based palladium IIP particles, while in MQ-based polymer it was via non-covalent mode. The AQ-based particles showed the best retention capacity (28.82 $\mu g\ g^{-1}$ of polymer) and the highest selectivity coefficient over platinum (5,500) and gold (674.2) ions. The complexes of $[PdI_4]^{2-}$ and $[Pd(SCN)_4]^{2-}$ with pyridinium ions were imprinted into polymeric network using 2-hydroxyethyl metacrylate as functional monomer (Daniel et al. 2006). The thiocyanate polymer with very high sorption capacity (41.6 $mg\ g^{-1}$) was used in a flow mode for the enrichment and separation of palladium in street dust samples.

The IIPs have been also prepared via imprinting ion-association complexes of Pd (II) with ammonium pyrrolidinedithiocarbamate (APDC), dimethylglyoxime (DMG), *N,N′*-diethylthiourea (DET) and 4-vinylpyridine into a polymeric network and studied for its selective preconcentration before determination by FAAS (Godlewska-Żyłkiewicz et al. 2010) and ETAAS (Godlewska-Żyłkiewicz et al. 2013) methods. The effect of the presence of potentially interfering ions (Cu(II), Ni (II), Cd(II), Zn(II), Pt(IV)) was neglible on the Pd-DMG polymers obtained with chloroform as a porogen, although this IIPs exhibited lower sorption capacity (9.3 $mg\ g^{-1}$) than Pd-DET (12.2 $mg\ g^{-1}$) and Pd-APDC (13.3 $mg\ g^{-1}$) (Godlewska-Żyłkiewicz et al. 2010). The authors decided to use Pd-DET imprinted polymer for separation of palladium from different environmental samples at pH 0.5–1, even though lower sorption capacity (2.4 $\mu g\ g^{-1}$) under these conditions was achieved. However, such media allowed selective enrichment of Pd(II) from certain matrix such as geological materials.

The complexes of platinum and ruthenium with thiosemibarbazides and their thiosemicarbazone derivatives were chosen as the template molecules in polymerization reaction for selective IIPs (Leśniewska et al. 2011; Zambrzycka et al. 2011, 2013). Better selectivity for Ru(III) in the presence of Pt(IV), Pd(II), Rh(III) and Co(II) ions as well as the higher sorption capacity (237.4 µg g^{-1}) was obtained for benzaldehyde thiosemicarbazone in comparison to other ruthenium imprinted polymers (Zambrzycka et al. 2013). The developed separation procedure was successfully applied to ETAAS determination of trace amounts of ruthenium in tap and river water, municipal sewage, road runoff and grass. Scheme for the preparation of IIP using Rh(III)-allyl acetoacetate complex as a template is presented in Fig. 3 (Godlewska-Żyłkiewicz et al. 2012). The use of this polymer has several advantages over IIPs based on imprinted Ru-TSd complex, including higher efficiency of analyte elution, procedure precision and shorter time of analysis. Despite its lower sorption capacity, this sorbent exhibited better selectivity, which is a result of the ligand chosen for rhodium complexation to form the template of the polymer. Table 1 summarizes the application of IIPs for enrichment and separation of PGEs from natural samples.

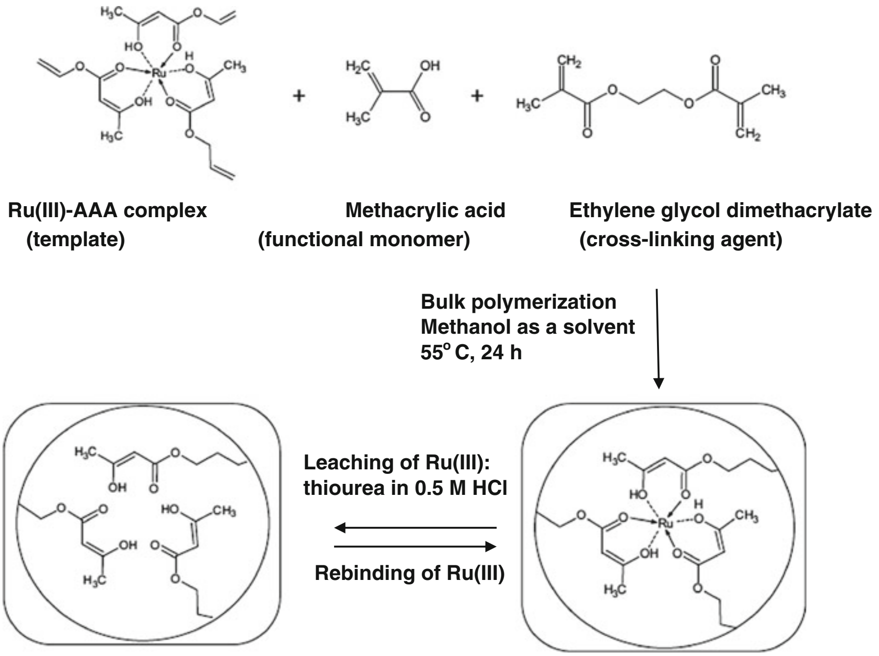

Fig. 3 Scheme of the preparation of Ru(III)-allyl acetoacetate imprinted polymer (Godlewska-Żyłkiewicz et al. 2012). Reproduced with permission from Elsevier

Table 1 Ion-imprinted polymers for platinum metal enrichment and separation

Sorbent	Sample pH	Eluent	Sorption capacity	LOD, µg L^{-1} (detection method)	Samples	Ref.
Pd(II)						
$[Pd(SCN)_4]^{2-}(VP)^+$	4	Methanol in 0.1 mol L^{-1} HCl	41.6 mg g^{-1}	1.5 (FAAS)	Street dust	Daniel et al. 2006
Pd-DGM-VP	6	0.3 mol L^{-1} TU in 1 mol L^{-1} HCl	9.3 mg g^{-1}	5 (FAAS)	Spiked tap water	Godlewska-Żyłkiewicz et al. 2010
Pd-DET-VP	0.5–1	0.5 mol L^{-1} TU in 0.5 mol L^{-1} HCl	2.4 µg g^{-1}	0.012 (ETAAS)	Tap and river water, grass, certified Pt ore (SARM 7 and SARM 76)	Godlewska-Żyłkiewicz et al. 2013
Pt(II), Pt(IV)						
Pt-AcTSn	0.5–1	0.3 mol L^{-1} TU in 0.3 mol L^{-1} HCl	4.56 µg g^{-1}	0.16 (ETAAS)	Tap water, tunnel dust, anode slime	Leśniewska et al. 2011
Ru(III)						
Ru-TSd Ru-AcTSn	7.5	0.2 mol L^{-1} TU in 0.2 mol L^{-1} HCl	150 µg g^{-1} 81 µg g^{-1}	0.16 0.25 (ETAAS)	Spiked water, sludge, grass, human hair	Zambrzycka et al. 2011
Ru-AAA	6.5	0.3 mol L^{-1} TU in 0.1 mol L^{-1} HCl	2.25 µg g^{-1}	0.32 (ETAAS)	Tap, river water, municipal and road sewage, grass	Godlewska-Zylkiewicz et al. 2012
Ru-BnTSn	8	0.3 M mol L^{-1} TU in 0.3 mol L^{-1} HC	237.4 µg g^{-1}	0.26 (ETAAS)	Tap, river water, municipal sewage, road runoff, grass	Zambrzycka et al. 2013

VP vinylpyridine; *DMG* dimethylglyoxime; *TU* thiourea; *DET N,N*'-diethylthiourea; *AcTSn* acetalaldehyde thiosemibarbazone; *TSd* thiosemicarbazide; *AAA* allyl acetoacetate; *BnTSn* benzylaldehyde thiosemicarbazone

5 Conclusions

The determination of platinum metal ions in environmental and geological samples is difficult due to the high concentration of interfering matrix components and the low content of these metals. Application of pre concentration/separation procedures utilizing solid phase extraction is able to minimize these problems in an elegant way. The recent developments in this area were presented and discussed.

The use of nano materials in the sample preparation procedures is a topic of growing interest in analytical chemistry. Their properties have been extensively exploited in different separation/enrichment techniques such as solid phase extraction, micro extraction and filtration. Whereas mono functional nano materials provide a single function, the preparation of core/shell nanoparticles has been a subject of much research as it allows different properties to be combined in one material. In the preparation of these multifunctional nano materials variable strategies are used to attain a combination of targeting specificity, magnetic properties and quantitative analysis capability. The surface modification of nano materials by functional molecules, particles or polymers can improve the separation and pre concentration efficiency as well as analytical selectivity. Ion imprinted polymers exhibit high selectivity towards the target ion due to a memory effect resulting from their preparation process.

References

Afzali D, Mostafavi A, Beitollah H (2010) Application of organo-nanoclay as a solid sorbent for rhodium complex separation and preconcentration. Microchim Acta 171:97–102

Afzali D, Jamshidi R, Ghaseminezhad S, Afzali Z (2012) Preconcentration procedure trace amounts of palladium using multiwalled carbon nanotubes sorbent prior to flame atomic absorption spectrometry. Arab J Chem 5:461–466

Augusto F, Hantao LW, Mogollón GS, Braga SCG (2013) New materials and trends in sorbents for solid-phase extraction. Trends Anal Chem 43:14–23

Bagheri A, Taghizadeh M, Behbahani M, Asgharinezhad AA, Salarini M, Dehghani A, Ebrahimizadeh H, Amini MM (2012) Synthesis and characterization of magnetic metal-organic framework (MOF) as novel sorbent, and its optimization by experimental design methodology for determination of palladium in environmental samples. Talanta 99:132–139

Balcerzak M (2011) Methods for the determination of platinum group elements in environmental and biological matrices. Crit Rev Anal Chem 41:214–255

Behbahani M, Bagheri A, Gorji T, Nabid MR, Sedghi R, Oskooie HA, Heravi MM (2013) Application of poly (*N*-phenylethannoloamine) modified MWCNTs as a new sorbent for solid-phase extraction of trace palladium ions in soil and water samples. Sample Prep 1:10–17

Branger C, Meouche W, Margallin A (2013) Recent advances on ion-imprinted polymers. React Funct Polym 73:859–875

Bystrzejewski M, Pyrzynska K (2013) Enhancing the efficiency of $AuCl_4-$ ion removal from aqueous solution using activated carbon and carbon nanomaterials. Mater Chem Phys 141:454–460

Chen L, Wang T, Tong J (2011) Application of derivatized magnetic materials to the separation and the preconcentration of pollutants in water samples. Trends Anal Chem 30:1095–1108

Choi HC, Shim M, Bangsaruntipb S, Dai H (2002) Spontaneous reduction of metal ions on the sidewalls of carbon nanotubes. J Am Chem Soc 124:9058–9059

Daniel S, Prem EJ, Prasada Rao T (2005) Preconcentrative separation of palladium using palladium(II) ion-imprinted polymer particles formed with different quinoline derivatives and evaluation of binding parameters based on adsorption isotherm models. Talanta 65:441–452

Daniel S, Praveen RS, Prasada Rao T (2006) Ternary ion-association complex based ion imprinted polymers (IIPs) for trace determination of palladium(II) in environmental samples. Anal Chim Acta 570:79–87

Das D, Gupta U, Das AK (2012) Recent developments in solid phase extraction in elemental speciation of environmental samples with special reference to aqueous solutions. Trends Anal Chem 33:35–45

Dobrowolski R, Kuryłło M, Reszko-Zygmunt J (2008) Study of the trace palladium enrichment mechanism on modified activated carbons with respect to analytical applications. Polish J Chem 82:255–262

El-Sheikh AH, Al-Jafari MK, Sweileh JA (2012) Solid phase extraction and uptake properties of multi-walled carbon nanotubes of different dimensions towards some nitrophenols and chlorophenols from water. Int J Environ Anal Chem 92:190–209

Farahani MD, Shemirani F, Gharehbaghi M (2013) Ferro fluid-based dispersive solid extraction of palladium. Talanta 109:121–127

Ghaseminezhad S, Afzali D, Taher MA (2009) Flame atomic absorption spectrometry for the determination of trace amount of rhodium after separation and pre concentration onto modified multiwalled carbon nanotubes as a new solid sorbent. Talanta 80:168–172

Godlewska-Żyłkiewicz B (2004) Pre concentration and separation procedures for the spectrochemical determination of platinum and palladium. Microchim Acta 189:189–210

Godlewska-Żyłkiewicz B, Leśniewska B, Wawreniuk I (2010) Assessment of ion imprinted polymers based on Pd(II) chelate complex for pre concentration and FAAS determination of palladium. Talanta 83:596–604

Godlewska-Żylkiewicz B, Zambrzycka E, Leśniewska B, Wilczewska AZ (2012) Separation of ruthenium from environmental samples on polymeric sorbent based on imprinted Rh(III)-allyl acetoacetate complex. Talanta 89:352–359

Godlewska-Żylkiewicz B, Leśniewska B, Wilczewska AZ (2013) Evaluation of ion imprinted polymers for the solid phase extraction and electrothermal atomic absorption spectrometric determination of palladium in environmental samples. Inter J Environ Anal Chem 93:483–498

Hu J, Pan J, Zhang K, Lian H, Li G (2013) Novel applications of molecularly-imprinted polymers in sample preparation. Trends Anal Chem 43:37–52

Hubicki Z, Wawrzkiewicz M, Wołowicz A (2008) Application of ion exchange methods in recovery of Pd(II) ions—a review. Chem Anal (Warsaw) 53:759–784

Jia YF, Xiao B, Thomas KM (2002) Adsorption of metal ions on nitrogen surface functional groups in activated carbons. Langmuir 18:470–478

Kononova ON, Leyman TA, Gavrilova VN, Konontsev SG, Kashirin DM (2010) Sorption of platinum and rhodium on carbon adsorbents from chloride solutions. J Porous Mater 17:351–358

Leśniewska B, Kosińska M, Godlewska-Żyłkiewicz B, Zambrzycka E, Wilczewska AZ (2011) Selective solid phase extraction of platinum on an ion imprinted polymers for its electrothermal atomic absorption spectrometric determination in environment al samples. Microchim Acta 175:273–282

Li Y, Huang YF, Jiang Y, Tian BL, Han F, Yan XP (2011a) Displacement solid-phase extraction on mercapto-functionalized magnetite microspheres for inductively coupled plasma mass spectrometric determination of trace noble metals. Anal Chim Acta 692:42–49

Li D, Chang X, Hu Z, Wang Q, Tu Z, Li R (2011b) Selective solid-phase extraction of Au(III), Pd (II) and Pt(IV) using activated carbon modified with 2,6-diaminopyridine. Microchim Acta 174:131–136

Li R, He Q, Hu Z, Zhang S, Zhang L, Chang X (2012) Highly selective solid-phase extraction of trace Pd(II) by murexide functionalized halloysite nanotubes. Anal Chim Acta 713:136–144

López-Lorento AI, Simonet BM, Valcárcel M (2011) Analytical potential of hybrid nanoparticles. Anal Bioanal Chem 399:43–54

Lucena R, Simonet BM, Cárdenas S, Valcárcel M (2011) Potential of nanoparticles in ample preparation. J Chromatogr A 1218:620–637

Mladeneva E, Karadjova I, Tsalev DL (2012) Solid-phase extraction in the determination of gold, palladium and platinum. J Sep Sci 35:1249–1265

Mohammadi SZ, Karimi MA, Hamidian H, Baghelani YM, Karimzadeh L (2011) Determination of trace amounts of Pd(II) and Rh(III) ions in Pt-Ir alloy and road dust samples by flame atomic absorption spectrometry after simultaneous separation and pre concentration on non-modified magnetic nanoparticles. Scientia Iranica 18:1636–1642

Myasoedova GV, Mokrodoeva OB, Kubrakova IV (2007) Trends in sorption pre concentration combined with noble metal determination. Anal Sci 23:1031–1039

Perez-Lopez B, Merkoçi A (2012) Carbon nanotubes and grapheme in analytical sciences. Microchim Acta 179:1–16

Pyrzynska K (2010) Carbon nanostructures for separation, pre concentration and speciation of metal ions. Trends Anal Chem 29:718–727

Pyrzynska K (2013) Use of nanomaterials in sample preparation. Trends Anal Chem 43:100–108

Ravelo-Perez LM, Herrera-Herrera AN, Hernadez-Borgez J, Rodrigez-Delgado MA (2010) Carbon nanotubes. Solid-phase extraction. J Chromatogr A 1217:33–42

Simanova SA, Shukarev AV, Lysenko AA, Grebennikov SF, Astashkina OV (2008) Adsorption of palladium, platinum, and gold chloride complexes by carbon fibers with various structures. Fibre Chem 40:365–375

To Z, Lu S, Chang X, Li Z, Hu Z, Zhang L, Tian H (2011) Selective solid-phase extraction and separation of trace gold, palladium and platinum using activated carbon modified with ethyl-3-(2-aminoethylamino)-2-chlorobut-2-enoate. Microchim Acta 173:231–239

Uheida A, Iglesias M, Fontás C, Hidalo M, Salvadó V, Zhang Y, Muhammed M (2006) Sorption of palladium(II), rhodium(III) and platinum(IV) on Fe_3O_4 nanoparticles. J Colloid Interface Sci 301:402–408

Vassileva P, Tzvetkova P, Lakov L, Peshev O (2008) Thiourcil modified activated carbon as a sorbent for some precious and heavy metal ions. J Porous Mater 15:593–599

Yin CY, Arona MK, Daud WMA (2007) Review of modifications of activated carbon for enhancing contaminant uptakes from aqueous solutions. Sep Purif Technol 52:403–415

Yuan CG, Zhang Y, Wang S, Chang A (2011) Separation and preconcentration of palladium using modified multi-walled carbon nanotubes without chelating agent. Microchim Acta 173:361–367

Zambrzycka E, Roszko D, Leśniewska B, Wilczewska AZ, Godlewska-Żylkiewicz B (2011) Studies of ion-imprinted polymers for solid-phase extraction of ruthenium from environmental samples before its determination by electrothermal atomic absorption spectrometry. Spectrochim Acta Part B 66:508–516

Zambrzycka E, Kiedysz U, Wilczewska AZ, Leśniewska B, Godlewska-Żyłkiewicz B (2013) A novel ion imprinted polymer as a highly selective sorbent for separation of ruthenium ions from environmental samples. Anal Meth 5:3096–3105

Zhang BT, Zheng X, Li HF, Lin JM (2013) Application of carbon-based nano materials in sample preparation. Anal Chim Acta 784:1–17

Zhou L, Xu J, Liang X, Liu Z (2010) Adsorption of platinum(IV) and palladium(II) from aqueous solution by magnetic cross-linking chitosan particles modified with ethylenediamine. J Hazard Mater 182:518–524

Voltammetric Analysis of Platinum in Environmental Matrices

Santino Orecchio and Diana Amorello

Abstract This article will summarize measurement data for Pt in different environmental samples obtained by the authors using a recently developed approach by voltammetric analysis. A fast accumulation of platinum and rhodium in the environmental and biological matrices has been observed in the last few years and concern has arisen about potential environmental and health risks. Voltammetry was used for the determination of Pt and Rh in airborne particulate collected in Palermo, Italy. Possible interferences by other environmental metals have also been evaluated. All samples show concentrations of Pt and Rh above average upper crust values. The Pt and Rh concentrations in particulate samples collected at four air quality monitoring sites within the urban area of Palermo (Italy), where the air pollution often reaches high levels, leading to traffic restrictions. The highest mean values of Pt and Rh concentrations (Pt = 13 pg/m^3, Rh = 9.8 pg/m^3 with peak values of 33 pg/m^3 and 19 pg/m^3, respectively) were recorded at the Unità d'Italia urban station, and the lowest at CEP (a neighborhood of the city of Palermo) station (Pt = 3.6 pg/m^3, Rh = 0.26 pg/m^3), considered as a background station.

1 Introduction

This article will summarize measurement data for Pt in different environmental samples obtained by the authors using a recently developed approach by voltammetric analysis.

Over the last 20–30 years there has been exceptional anthropogenic contamination of environmental matrices and in particular urban atmosphere, prevalently attributed to the combustion of fossil fuels. The combustion of fuel inside the vehicle engine causes the emission of unburned hydrocarbons, carbon monoxide, nitrogen oxides, sulphur oxides, particulate, metals (Orecchio and Amorello 2011)

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and organic compounds (Orecchio 2007; Gianguzza et al. 2008) in the environment. The metals most implicated in this worldwide-level atmospheric pollution event are Platinum Group Elements (PGEs) released from catalytic converters (Orecchio and Amorello 2010, 2011) and V which is the most abundant metal present in crude oil, commonly in concentrations that exceed 1000 ppm. The PGEs, sometimes referred as the Platinum Group Metals (PGMs), comprise the rare elements such as platinum, palladium, rhodium, ruthenium, iridium and osmium.

In Europe, today, gasoline or petrol (lead free), diesel and, in few cases, liquefied petrol gas are the most common fuels used in cars. With the elimination of lead compounds from automotive fuels, the possibility of using this element as a marker of automotive traffic has been eliminated. Therefore, interest in new markers has moved to other elements.

Platinum is naturally occurring element, present in relative very low concentrations (Pt 0.01 = ppm) in the earth crust (Greenwood and Earnshaw 1985) and therefore in environmental matrices (water, soil, sediment, organism, etc.) (Orecchio and Amorello 2011) and derived atmospheric particulate matter (Zereini et al. 2001; Wiseman and Zereini 2009).

In the past, PGMs were considered to be relatively inert, but some recent researches have demonstrated the biological availability of these elements as soluble species (Ek et al. 2004; Hoppstock and Sures 2004): in fact, studies with mussels and plants exposed to road dust showed an unexpectedly high bioaccumulation of PGMs (Sures et al. 2001). The high concentrations of platinum found in environmental matrices reveal the fundamental contribution from human activities (Konig et al. 1992; Orecchio et al. 2012; Rubino et al. 2009), especially automotive traffic, since PGEs are widely used in catalytic converters.

Generally, authorities use the values of concentrations of particulate matter in urban air to make decisions about the traffic restrictions in city centers. This approach, in our opinion, is not correct, because the sources of particulate matter, in European cities, can be manifold, while platinum is originated, at the present time, only by the catalytic converters. Consequently, our researches are aimed at a contribution to a monitoring of platinum utilized as marker for pollution caused by motor vehicle traffic. This requires the development of good analytical methods to measure very low Pt concentrations in complex environmental matrices, as well to estimate background concentrations.

At the present time, literature data concerning direct measurements of the emitted PGE are limited to some papers, in particular, Pt, Pd and Rh have been detected in particles directly from the exhaust gas by complicated and expensive techniques as X-ray photoelectron spectroscopy analysis (XPS) and by high-resolution ICP-MS (Moldovan et al. 1999; Petrucci et al. 2000; Vlasankova et al. 1999).

The main purpose of our researches is to develop reliable methods for the determination of PGMs at trace level in the solutions obtained from the mineralization of environmental matrices, because they cannot be readily measured using conventional techniques used in most laboratories, in particular, the ICP-OES and ICP-MS techniques: in these cases, determinations are problematic, due to difficulties connected to the isolation of these metals from the matrix and to strong interferences which cannot be eliminated (Zimmermann et al. 2001); as a consequence, alternative methods should be preferred.

Previous studies (Orecchio and Amorello 2010) were aimed at a contribution to a monitoring of platinum in particular in organisms considered bioaccumulators because very little is known about the influence of these elements on organisms exposed to this type of contamination. Biomonitoring methods using organisms, or part of them, offer a feasible low cost alternative, especially in terms of high spatial resolution and time-averaged data series. The advantages of biomonitoring to evaluate environmental quality are reported in some articles (Culotta et al. 2002, 2005; Orecchio 2007; Lombardo et al. 2001; Dongarra et al. 2003).

In this work are presented results about monitoring of PGE, in particular Pt and Rh in several environmental matrices, as soil and leaves because very little is known about the levels of these metals in urban areas. Moreover, new and original results about the concentration of PGE in atmospheric particulate collected in Palermo are here presented and discussed.

We used *Differential Pulsed Voltammetry* (DPV) and *Adsorbitive Stripping Voltammetry* (AdSV) to measure the concentrations of Pt and Rh respectively in solutions obtained from several environmental matrices. Theory and applications of voltammetry are given in references (Skoog and Leary 2000; Harris 2005). Historically, the voltammetry developed from the discovery of polarography in 1922 by Jaroslav Heyrovsky for which he received the 1959 Nobel Prize. The voltammetric technique involves the application of a potential (*E*) to a working electrode and the monitoring of the resulting current (i) flowing in the electro-chemical cell. In many cases the applied potential is varied or the current is measured over a period of time (*t*). The analytical advantages of the voltammetric techniques consist of exceptional sensitivity, specificity, with large useful linear concentration range for several inorganic and organic compounds (10^{-12}–10^{-3} M), high precision (<1 %), wide dynamic range, a large number of useful solvents and electrolytes, possible simultaneous analysis of different compounds, the ability to determine kinetic and mechanisms of reaction and fast analysis times. In fact, once the sample has been prepared (mineralized, in the cases of solids, organisms, etc.), the voltammogram can be acquired quickly.

In the *differential pulse voltammetry,* utilized by us for the analysis of platinum, the potential is scanned with a series of pulses (from 10 to 100 mV) which are superimposed on a linearly increasing potential. The current is measured immediately before the application of the pulse and at the end of the pulse. The difference between current at these points for each pulse is measured and plotted against the base potential (Kounaves 1997). In this way, the analytical signal is free from non faradic (charging) current. Analysis of Rh was performed with Adsorptive stripping voltammetry. A metal complex adsorbed at the working electrode, gives a signal by scanning the electrode potential, usually in a reductive direction. Since this is a surface technique, it is appropriate for determining ultra-trace levels of metals.

There are many applications of voltammetry for the determination of different metals in different matrices (Piech et al. 2008; Stoica et al. 2004), but to the best of our knowledge, there are few reports on the application of the electrochemical method for the determination of ultra traces of Pt in complex such as environmental matrices (Orecchio and Amorello 2010, 2011; Orecchio et al. 2012; Locatelli 2006).

2 Previous Our Researches

In the case of soil (Orecchio and Amorello 2011), speciation of Pt was performed in samples collected from 24 stations: a sequential treatment at first in HNO_3 and successively aqua regia allowed us to separate respectively two fractions of Pt: oxides and/or others compounds and metallic platinum. Concentrations of total Pt in surface soils were in the ranges from 0.6 to 2240 μg/kg d.w. while, in the lower soil from 0.3 to 16 μg/kg d.w. (Orecchio and Amorello 2011) The lowest values of total Pt were found in the less contaminated stations, taken as references, while the highest concentrations were measured in two road near train and bus stations in the centre of Palermo characterized by slow and heavy traffic flow (Orecchio and Amorello 2011). The results of this paper show that Pt concentrations in soils are always enhanced in the uppermost horizon and decline to background values by a depth of 10 cm. In analyzed samples platinum exists principally in the metallic form.

In another study (Orecchio and Amorello 2010), leaves of *Nerium oleander* have been chosen as bioaccumulators for platinum and rhodium because the plant (evergreen) is widespread both in metropolitan and in the peripheral areas of the cities. Concentrations of platinum ranged from 0.33 to 25 μg/kg d.w. Also in this case, the higher concentrations of both metals were detected in samples from the urban area of Palermo compared to the control sites and are diagnostic of conspicuous air contamination. In this research (Orecchio and Amorello 2010), with the aim to assess the reliability of oleander leaves as bioaccumulator of air pollutants, we also carried out a linear regression analysis between total PAHs concentrations in oleander leaves measured in a previous study (Culotta et al. 2005) and the concentrations of platinum in the same type of leaves. The high correlation demonstrates that oleander leaves can be used as indicators of PGE contamination. Likewise, a good correlation was found between total PAHs concentrations in leaves of Quercus (Orecchio 2007) and the concentrations of platinum in the leaves of oleander measured. We presuppose that the high correlation with contaminant of the same origin (traffic) demonstrates that oleander leaves can be used in order to estimate easily and fast, air quality of a chosen region. The high correlation of the content of Pt in the soils of Palermo stations (Orecchio and Amorello 2011) and the concentration of the same element in leaves of *Nerium oleander* confirms the geographical distribution of the considered contaminant in the area of Palermo. We can conclude that despite the commonly accepted fact that platinum vehicular emission takes place in metallic and oxide forms (Palacios et al. 2000; Zereini and Alt 2000), we can speculate that at least part of the particles is soluble, and over a period of time can transform in contact with various kinds of compounds in the environment, and in particular on leaves surface, thus providing platinum compounds ready to enter in the vegetal organism or in part of them and in the food chain.

3 New Monitoring: Assessment of Airborne Platinum and Rhodium Associated with the Atmospheric Particulate in the Palermo (Italy) Area; Analytical Method Using Voltammetry

3.1 Experimental

3.1.1 Quality Assurance

In our researches we assure the quality of results following several precautions. All the vessels and flasks are cleaned before use by rinsing three times with HNO_3 (2 %) and three times with redistilled Milli-Q water. Procedural blanks are routinely analysed every four-five samples, using the same procedure as for the samples, and the calculated mean concentrations for the element are then subtracted from results of each sample. Since certificate particulate samples are often not available, the analytical procedure is checked for accuracy by analysing the enriched samples prepared by us. Samples of matrices containing Pt below the detection limits are spiked with a known quantity of Pt and analysed. Generally, the average recoveries of added pollutants ranged from 70 to 105 %, with relative standard deviations less than 10 %. The quantification limit (LQ) is estimated as 10 s (ten times the background noise) (IUPAC criterion).

3.1.2 Chemicals

Standard stock solution of Pt and Rh (1000 mg/mL) were purchased from Fluka (Milano, Italy), the diluted solutions were prepared daily. The reagents used throughout were analytical grade (Carlo Erba, Milano, Italy) and all solutions were prepared in Milli-Q water. HNO_3 (65 %), H_2SO_4 (96 %) and HCl (37 %) were analytical grade (Suprapur Carlo Erba, Milano, Italy). Hydrazine 1.8 mM/L and formaldehyde (0.6 mM/L for Pt and 0.02 mM/L for Rh) solutions were prepared daily from analytical grade reagents (Carlo Erba, Milano, Italy).

3.1.3 Sampling and Site

We have taken into account Palermo, as representative of the majority of European cities. Palermo, a city in southern Italy, has warm weather and high relative humidity throughout the year.

In terms of vehicular traffic and activities, Palermo, is similar to most European cities. Our previous studies (Orecchio and Amorello 2011; Orecchio 2007, 2010; Gianguzza et al. 2008; Lombardo et al. 2001) indicate that the air in Palermo is gravely polluted, mainly from traffic. Total suspended particles (TSP), present at high levels, contain large amount of contaminants with differences in terms of concentration and profiles of organic contaminants (PAHs) with localization, in the air adjacent to a busy street.

In the city of Palermo, Amia (municipal air quality monitoring network) has installed nine monitoring stations that measure the levels of environmental pollution. The results of monitored parameters (PM_{10}, NO_x, SO_2, CO, O_3) are available on a web site (http://www.palermoweb.com) from 2003 to today. No metal is directly monitored by the monitoring units.

Forty-three particulate samples were collected also collected in December 2010, at five sampling stations (Fig. 1) belonging to the municipal air quality monitoring network (AMIA), characterized by varying traffic density. In order to determine very low concentrations of both metals, each sample was obtained by mineralizing at least three filters at each station. Four monitoring stations are close to roads with a high density of vehicles; the fifth is located in a suburban site. The selected stations were:

Giulio Cesare: a large square in front of the railway station exposed to heavy traffic, composed by cars, urban and extra-urban buses. It is about one kilometre from marine coast. Number of samples collected: 5;

Castelnuovo: large square, located in city centre and exposed to heavy traffic, composed by cars and urban buses, especially during week end and festivity. Number of samples collected: 5;

Unità d'Italia: a large square, exposed to heavy traffic density. Number of samples collected: 15;

Fig. 1 Location of sampling sites

De Blasi: the station is located close to a large and ventilated crossroads with traffic lights at pedestrian crossings, and is characterised by high traffic flows, consisting of cars, heavy-duty vehicles and buses.

CEP: a sub-urban background station without any direct influence of urban activities (car traffic). This site was selected as a control, to monitor the background level of the two elements. Number of samples collected: 9.

Sampling was performed according to European Standard EN12341: samples were collected using a sampler (Explorer or mod. ZB1, Zambelli, Italy), a sampling inlet head (Zambelli), operating at a constant sampling rate of 38.3 l/m (2.3 m^3/h). The sampling time was 24 h, from midnight to midnight. Particles were collected on a quartz or glass fibre filter (47 mm in diameter). Initial and final weighing of filters were carried out in a temperature and humidity controlled room (T = 20 ± 1°C, RH = 50 % ± 5 %), after conditioning the filters for 48 h before and after sampling. Gravimetric determination of the particulate was carried out by three successive weight measurements using an analytical microbalance Sartorius ME5-OCE.

3.1.4 Treatment of Samples

The mineralization was carried out by digesting each sample in 3–10 ml of hot HNO_3 + HCl (1:3) (Suprapur quality) in a Milestone model MLS-1200 Mega (Milestone Laboratory Systems, Italy) microwave oven (1000 W maximum power) equipped with six high-pressure (up to 100 bar) Teflon containers. The operating parameters for the microwave digestion are: 1 min at 200 W, 1 min at 0 W, 5 min at 250 W, 5 min at 400 W, 3 min at 600 W and 5 min at 300 W. After digestion was completed, the clear, colourless solution was transferred into a volumetric flask and brought to volume with water purified by Milli-Q system.

3.1.5 Voltammetric Analysis

The solutions obtained from the acid treatment were analyzed by *differential pulse voltammetry* (DPV/a) and AdSV for Rh using a Polarograph Amel Model 433-A with a hanging mercury drop electrode (HMDE) as working electrode, and a auxiliary glassy carbon electrode, and a Ag/AgCl/KCl (sat.) as reference electrode. The instrumental parameters for analysis are shown in Tables 1 and 2.

At the start of each measure, the solutions obtained from mineralization are degassed with analytical grade nitrogen (99.998 %) for 300 s and a flow of nitrogen is maintained over the solution during the measure to prevent oxygen interference. The experiments generally are performed at constant temperature (25 °C). Platinum determinations are carried out in aqueous H_2SO_4 1 M as supporting electrolyte, in the presence of 1.2 mM hydrazine sulphate and 0.6 mM formaldehyde. Formaldehyde and hydrazine condense in solution to form the corresponding hydrazone,

Table 1 Operating parameters for the voltammetric analysis of the solutions obtained from particulate samples

Analytes	Tecniques	Electrolytes	Reagent
Pt	DPV/a	H_2SO_4 1 M	$[N_2H_4] = 1.8$ mmol L^{-1}, $[H_2CO] = 0.6$ mmol L^{-1}
Rh	DPSAV	HCl 0.42 M	$[H_2CO] = 0.02$ mol L^{-1}

Table 2 Instrumental parameters for the voltammetric analysis of the solutions obtained from particulate samples

Parameters	Pt	Rh
Initial potential (mV)	−300	−900
Final potential (mV)	−1000	−1200
Current range	Automatic	Automatic
Potential scan rate (mV/s)	50	10
Potential of deposition (mV)	–	−700
Cycle n°	1	1
Deposition time (s)	–	30
Stirring rate (rpm)	300	300
Size of the drop (a.u.)	60	60
Delay time before potential sweep (s)	10	10

which forms a complex with platinum. Subsequently, a potential changing from −0.3 to −1.0 V in the differential pulse mode is applied to the working electrode, and the catalytic current of the hydrogen formation is measured at −0.85 V (vs. Ag/AgCl) (Fig. 2). The current intensity results proportional to Pt concentration. The catalytic effect of Pt makes the analysis very sensitive.

Adsorptive stripping voltammetry was used for analysis of Rh. This technique is well-known to provide an excellent sensitivity for a variety of trace metals at a mercury electrode (film or drop); it involves complexation of metals with specific ligands and adsorption of the related complex on the mercury surface. The adsorbed complex is electrochemically removed by scanning the electrode potential, usually in a reductive direction. Since this is a surface technique, it is appropriate for determining ultra-trace levels of metals in solutions. In hydrochloric acid solution (0.42 M), in the presence of formaldehyde (0.02 M), a complex rhodium–formaldehyde is adsorbed on a hanging mercury electrode at −0.7 V. The potential of working electrode was then changed from −0.9 to −1.2 V, giving a peak at −1.1 V due to hydrogen reduction, catalyzed by Rh formaldehyde complex. The catalytic effect of Rh explains the great sensitivity of this method. The operating parameters for both metals are reported in Tables 1 and 2.

Voltammetric curves of standard solutions are reported respectively in Figs. 2 and 3. For both analita, quantitative analyses were performed using the standard

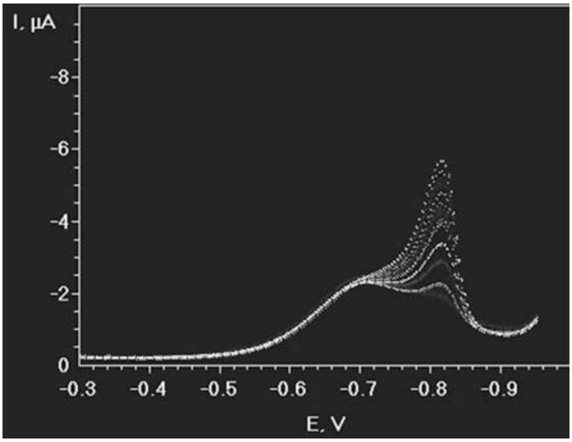

Fig. 2 Voltammetric curves of platinum

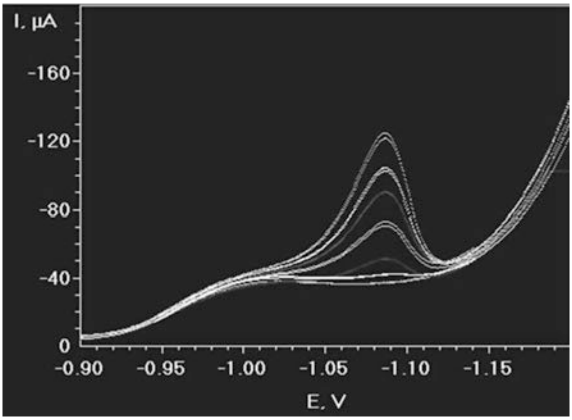

Fig. 3 Voltammetric curves of rhodium

addition method. Calibration graphs were built using data from measurements and evaluated by the least squares linear regression method. Under the optimum conditions a very good linear correlation was obtained between the monitored voltammetric peak current and metals concentrations. As an example, the calibration curves for platinum and rhodium are shown in Figs. 4 and 5.

4 Results and Discussion

The developed voltammetric method showed high sensitivity and very elevated reproducibility. The detection limits for Pt and Rh are, respectively, 1.1 and 0.08 pg/m^3; the precision, expressed as relative standard deviation (RSD %) was 4 % for Pt and 3 % for Rh.

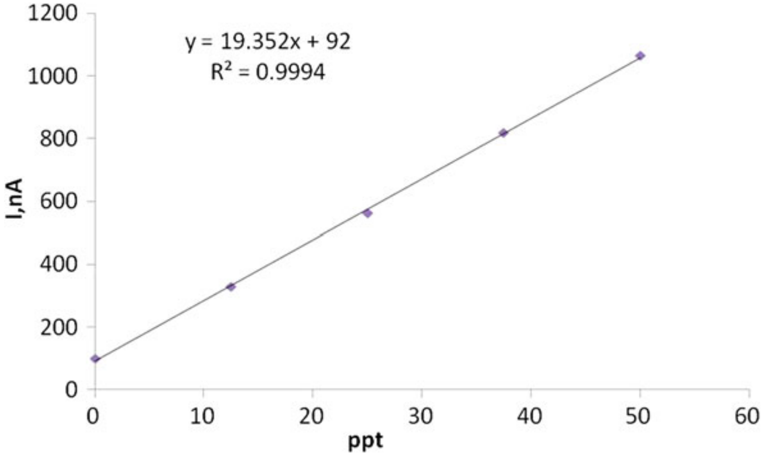

Fig. 4 Calibration graphs for Pt constructed using standard addition procedure and evaluated by the least-squares linear regression method

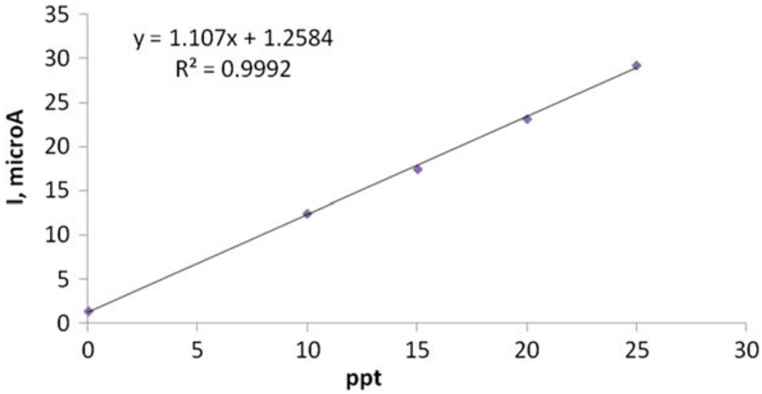

Fig. 5 Calibration graphs for Rh constructed using standard addition procedure and evaluated by the least-squares linear regression method

The mean concentration for platinum and rhodium in particulate samples, collected in Palermo area, not considering the reference station, were respectively 10.6 and 7.5 pg/m^3. Pt concentrations ranged from 1.1 to 33 pg/m^3, while Rh concentrations were in the range 0.08–19 pg/m^3 (Table 3, Fig. 5). For rhodium, in many cases the analyses of the particulate samples fall below the detection limits. In almost all samples, platinum is more abundant than rhodium.

The highest mean value of Pt and Rh concentrations (13 and 9.7 ng/m^3) were registered at Unità d'Italia station, located in an area of Palermo characterized by slow and heavy traffic flow, in particular during the opening time of offices and shops

Table 3 Platinum and rhodium concentrations in pg/m^3 measured on particulate collected in Palermo area

Samples	Pt (pg/m^3)	Rh (pg/m^3)	Volume (m^3)	Particulate (mg)
G. Cesare 1	10	2.1	104.9	2.64
G. Cesare 2	3.6	1.7	154.7	5.10
G. Cesare 3	5.6	1.5	155.6	5.90
G. Cesare 4	4.9	3.3	155.8	4.16
G. Cesare 5	4.4	3.2	104.2	4.91
Castelnuovo 1	8.5	8.1	156.8	2.56
Castelnuovo 2	2.0	1.0	102.6	1.90
Castelnuovo 3	25	18	140.9	2.04
Castelnuovo 4	3.6	1.0	158.1	2.48
Castelnuovo 5	3.6	1.0	104.8	1.62
Un. Italia 1	25	12	130.3	3.92
Un. Italia 2	10	9.2	163.3	6.26
Un. Italia 3	5.6	5.2	162.8	3.63
Un. Italia 4	8.0	7.8	162.7	4.56
Un. Italia 5	7.4	7.1	162.4	7.09
Un. Italia 6	13	12	162.2	6.90
Un. Italia 7	12	11	162.1	5.81
Un. Italia 8	16	15	162.1	5.03
Un. Italia 9	5.4	3.5	156.4	4.82
Un. Italia 10	8.3	5.0	156.6	4.70
Un. Italia 11	33	19	210.8	9.23
Un. Italia 12	24	19	157.2	6.65
Un. Italia 13	5.4	7.8	155.1	3.26
Un. Italia 14	4.6	4.1	104.2	3.23
Un. Italia 15	17	9.0	104.0	2.63
De Blasi 1	11	7.0	103.0	2.21
CEP 1	<1.1	<0.08	155.9	4.36
CEP 2	<1.1	<0.08	156.3	4.80
CEP 3	<1.1	<0.08	156.7	4.72
CEP 4	<1.1	<0.08	157.3	3.80
CEP 5	<1.1	<0.08	157.5	4.46
CEP 6	<1.1	<0.08	104.4	3.11
CEP 7	<1.1	<0.08	152.5	3.15
CEP 8	<1.1	<0.08	156.9	7.60
CEP 9	<1.1	<0.08	155.2	2.79

(8.00–20.00), while, the lowest values was found at CEP (<1.1 and 0.08 ng/m^3), considered as a sub-urban background station because far from emissions from vehicular traffic. With regard to this station, it is useful to note that the mean particulate concentration (28.7 μg/m^3), recorded during the present study, is not significantly different from those observed in other stations (29.5 μg/m^3) where concentrations of analita are higher. These apparent anomalies probably are related to wind transport of dust toward the Mediterranean area (Fig. 6).

The wide range of Pt and Rh concentrations (relative standard deviations if all the stations are taken into account were 86 % for Pt and 103 % for Rh) indicates heterogeneous levels of contamination in the investigated area. These results suggest that the fluctuation in the concentration of Pt and Rh is directly linked to the traffic conditions at least nearby the roads. Furthermore, we note that variations at same site are very large. This variability may be explained by the different intensity of auto vehicular traffic emissions in different days and also by the changing meteorological conditions of the area.

The highly non-homogeneous distribution of Pt and Rh in the different stations was found to be very different from that of the particulate (RSD = 32 %) measured by AMIA (http://amianet.com) in the investigated area. The concentrations of Pt and Rh are highly correlated (r = 0.93), suggesting their common origin (Fig. 7), but they are not correlated with the concentrations of particulate. This evidence is in good agreement to results obtained in previous papers (Orecchio and Amorello 2010, 2011) and can be explained by assuming that a fraction of particulate, in a city like Palermo, has different origin than that of Pt and Rh, which can be attributed exclusively to vehicle traffic. In fact, a recent paper (Dongarra et al. 2003) demonstrates that at Palermo traffic emissions have an important effect on both PM_{10} and $PM_{2.5}$ mass levels. About 50 % of particulate matter is from road traffic. It is also documented (Dongarra et al. 2003) that in roads with high densities of traffic, atmospheric particulates loads may be up to about 140 % higher than in suburban sites.

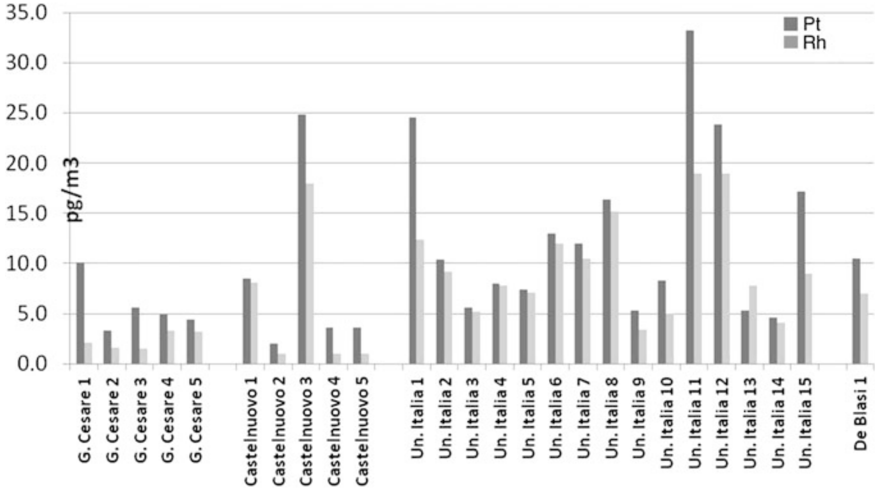

Fig. 6 Platinum and rhodium concentrations measured on particulate samples collected in Palermo area

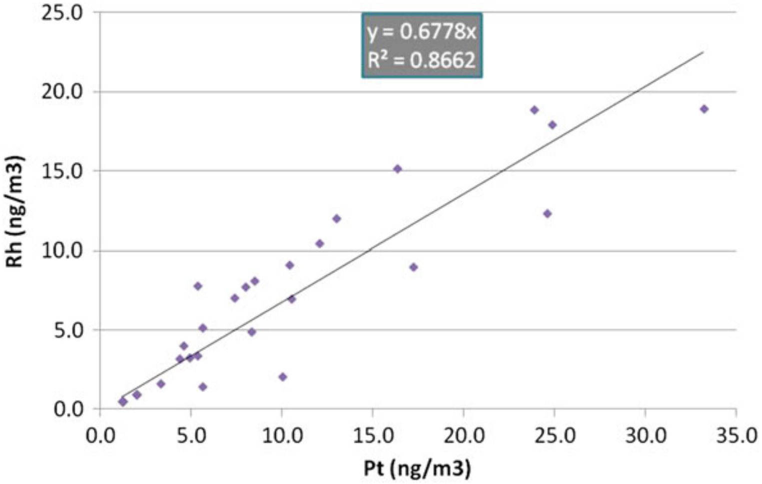

Fig. 7 Correlation between Pt and Rh determined in the particulate sampled in Palermo area

A comparison between the Pt and Rh in airborne particulate presented here with the ones from the literature is only possible for those from limited areas, because of the lack of Pt and Rh determinations. For example, in Munich, was measured only the concentration of platinum (21.5 pg/m^3) that was significantly greater than those of other sites listed below. Platinum and rhodium concentrations measured in Palermo area fall into the range of literature data, which we report in Fig. 8. For example, some researchers (Ek et al. 2004; Rauch et al. 2001, 2005, 2006) measured PGE concentrations in particulate in two different sites in Göteborg, Sweden. For the high traffic site, it was found to contain a mean of 14 pg/m3 of platinum and 2.9 pg/m^3 of rhodium. In Madrid, Pt content varied according to position of stations and associated traffic intensities from 7.3 to 18 pg/m^3 (Gomez et al. 2001), while Rh was in the range from 2.8 to 4.6 pg/m^3. In samples collected from a site with a heavy traffic load in Frankfurt, Pt, and Rh concentrations ranged from 5.2 to 15.7 pg/m^3 and 0.8 to 3.9 pg/m^3, respectively (Wiseman and Zereini 2009). In Rome, Pt content varied from 8.1 to 8.6 pg/m^3, while Rh was in the range from 2.2 to 3 pg/m^3. In Mexico City the concentrations of the two metals were 9.3 and 3.2 pg/m3 respectively.

We found a Pt/Rh ratio about 1.5. In literature the values of ratios are highly variable (Wiseman and Zereini 2009). Our ratio is in agreement to the data obtained from Moldovan (Moldovan et al. 1999) who affirm that for the fresh Pt–Pd–Rh gasoline catalysts the particulate release was: 112 ng/km of Pt and 77 ng/km of Rh; for Pd–Rh gasoline catalyst the release was of 43 and 12 ng/km of Pt and Rh respectively; After ageing (30,000–80,000 km), the particulate release for the first type of gasoline catalyst was: 8.3 ng/km of Pt and 2.5 ng/km of Rh and 5.4, and 2.2 ng/km of Pt and Rh, respectively for the Pd–Rh converter.

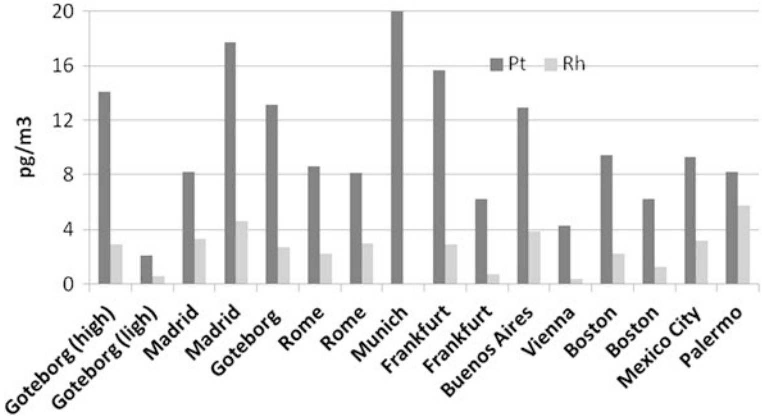

Fig. 8 Pt and Rh concentrations in airborne particulate of different country

The concentrations of Pt and Rh in the samples from all sites exceed by far natural concentrations. In order to assess the contribution of anthropogenic emissions within the urban area, enrichment factors (*EF*) were computed with respect to the upper continental earth crust (Greenwood and Earnshaw 1985). The *EF* values calculated for each sample are shown in Fig. 9 according to the following algorithm:

$$EF_a = (Xa)_{Station}/(Xa)_{background}$$

where Xa is the concentration of the analita in particulate (mg/kg).

The highest values of EF (1249 and 172), for platinum and rhodium, were observed in Castelnuovo station, in the period between 24 and 26 December. This finding is in agreement with the fact that before and during festivity, the vehicle traffic, especially in the commercial area of Palermo, is very intense, while the lowest one (7.4 and 5.4) were detected in the CEP station.

In good agreement to Dongarrà (Dongarra et al. 2003), trace elements (Pt and Rh in our case) supposed to be introduced into the environment principally by anthropogenic activities (in our case only by vehicular traffic because there are no other sources of platinum and rhodium in the investigated area) were highly enriched with respect to local soil. Pt and Rh, which have high EF values, thus reveal them potential use as a fingerprint, to identify the contribution of motor vehicles to traffic-derived particulate matter.

To compare the total metals content at the different sampling sites, the metal pollution index (MPI) was used, obtained with the equation:

$$\text{MPI} = (C_{Pt} * C_{Rh})^{1/2}$$

where C_{Pt} and C_{Rh} = concentration of the single metal in the sample. The values of MPI (Fig. 10) ranged from 1 determined in background station to 21–25 determined in

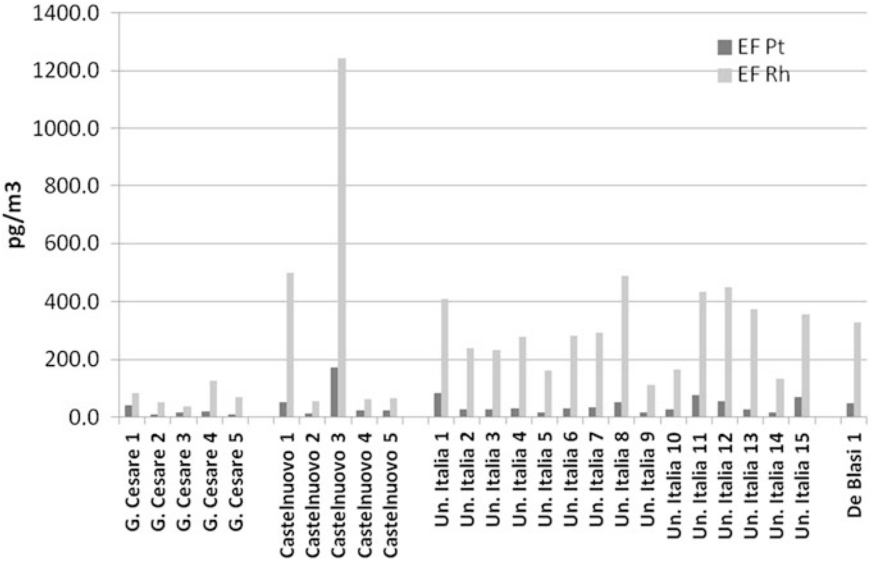

Fig. 9 Enrichment factors for Pt and Rh

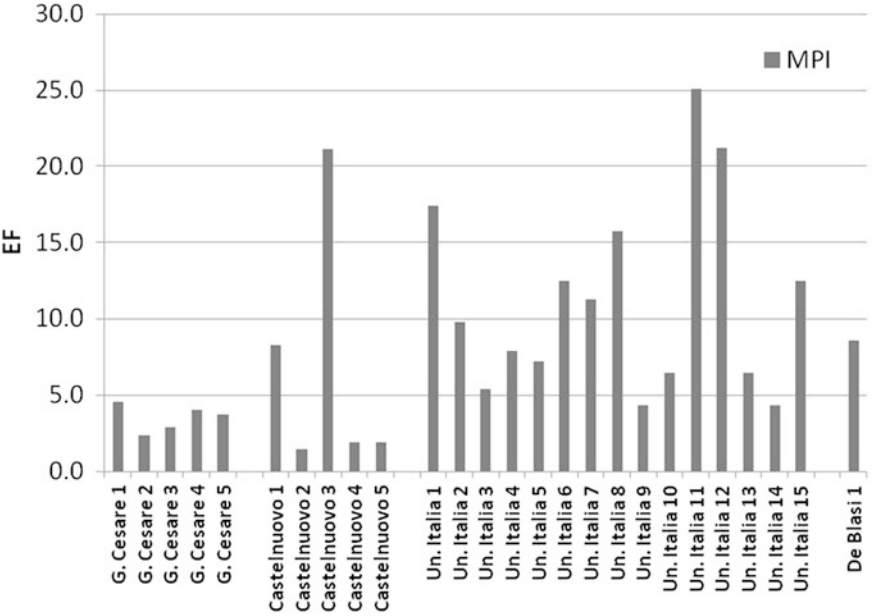

Fig. 10 Metal pollution index for investigated station

the Castelnuovo and Unità d'Italia stations, located in areas with high vehicular traffic, in particular, during opening the time of offices and shops (from 8.00 to 20.00).

Differences of Pt and Rh concentrations in stations between sub-urban and road and anthropized areas are in agreement with differences in others contaminant (PAHs) contents measured in the same area in soils.

5 Conclusions

The present study demonstrates that the voltammetric analysis of Pt and Rh in the atmospheric particulate is an excellent method for determination of trace amounts of Pt and Rh. Finally, the above system offers a practical potential for the subsequent determination of platinum and rhodium without any interference due to other species present in the matrix with similar reduction potential. The represented method includes advantages of high sensitivity, high selectivity, simplicity, speed and low costs.

Data here reported constitute the results of the first monitoring campaign of platinum and rhodium concentration levels in atmospheric particulate collected at Palermo. The higher amounts of analita which are detected in stations located in the urban areas of Palermo compared to the control site samples are diagnostic of conspicuous air contamination in particular in zones with heavy traffic. The levels of two metals are similar to those measured for European and American large cities.

Based on the results of the study by some researchers (Merget 1999; Merget and Rosner 2001) the level of Pt in the investigated area, at the present, may be defined as safe because lower 100 ng/m^3. With regard to the sensitizing potential, there is no data that other PGE show a higher potency than Pt compounds.

This work demonstrates that traffic emissions have not an important impact on the particulate levels. Thus, we expect that data as the one reported here can be considered as reference works for further investigations in the region, where there is a lack of systematic studies on unusual metals in atmospheric particulate.

Considering that the proportion of new cars using converters will increase it is necessary to carry out researches on the transformation of PGE in organisms and in natural matrices.

The results on air quality in the city of Palermo obtained in this research using Pt and Rh are in agreement with results of other studies that measured other environmental contaminants.

Considering that Pt and Rh, in an urban area are emitted only by auto vehicular traffic and considering that concentrations of analita are not correlated with the level of particulate we can deduce that only a fraction of particulate can be attributed exclusively to vehicle traffic. This conclusion is very important because, in Italy and in other countries, the use of cars in urban areas is often prohibited when particulate concentrations exceed a certain threshold and therefore it would be necessary to use other indicators of pollution from traffic to formulate decisions on the limitation in the use of private cars.

References

Culotta L, Melati MR, Orecchio S (2002) The use of leaves of Rosmarinus officinalis L. as samplers for polycyclic aromatic hydrocarbons. Assessment of air quality in the area of Palermo. Ann Chim 92:837–845

Culotta L, Gianguzza A, Orecchio S (2005) Leaves of Nerium oleander L. as bioaccumulators of polycyclic aromatic hydrocarbons (PAH) in the air of Palermo (Italy). Extraction and GC–MS analysis, distribution and sources. Polycycl Aromat Compd 25:327–344

Dongarra G, Varrica D, Sabatino G (2003) Occurrence of platinum, palladium and gold in pine needles of Pinus pinea L. from the city of Palermo. Appl Geochem 18:109–116

Ek KH, Rauch S, Morrison GM, Lindberg P (2004) Platinum group elements in raptor eggs, faeces, blood, liver and kidney. Sci Total Environ 334(335):149–159

Gianguzza A, Culotta L, Orecchio S (2008) Absorption of polycyclic aromatic hydrocarbons by pinus bark: analytical method and use for environmental pollution monitoring in the Palermo area (Sicily, Italy). Environ Res 107:371–379

Gomez B, Gomez M, Sanchez JL, Fernandez R, Palacios MA (2001) Platinum and rhodium distribution in airborne particulate matter and road dust. Sci Total Environ 269:131–144

Greenwood NN, Earnshaw A (1985) Chemistry of the elements. Pergamon, Oxford, UK

Harris DC (2005) Chimica analitica quantitativa. Zanichelli, New York

Hoppstock K, Sures B (2004) Platinum group metals. In: Merian E, Anke M, Ihnat M, Stoeppler M (eds) Elements and their compounds in the environment. Wiley, Weinheim, pp 1047–1086

Konig HP, Hertel RF, Koch W, Rosner G (1992) Determination of the platinum emissions from threeway catalyst-equipped gasoline engine. Atmos Environ 26:741–745

Kounaves SP (1997) Voltammetric techniques (Chap. 37). In: Settle FA (ed) Handbook of instrumental techniques for analytical chemistry. Prentice Hall, Upper Saddle River, USA. http://www.prenhall.com/settle/chapters/ch37.pdf

Locatelli C (2006) Simultaneous square wave stripping voltammetric determination of platinum group metals (PGMs) and lead at trace and ultra trace concentration level, application to surface water. Anal Chim Acta 557:70–77

Lombardo M, Melati MR, Orecchio S (2001) Assessment of the quality of the air in the city of Palermo through chemical and cell analyses on Pinus needles. Atmos Environ 35:6435–6445

Merget R (1999) Occupational platinum salt allergy. Diagnosis, prognosis, prevention and therapy. In: Zereini F, Alt F (eds) Anthropogenic platinum-group-element emissions and their impact on man and environment. Springer, Berlin, pp 257–266

Merget R, Rosner G (2001) Evaluation of the health risk of platinum group metals emitted from automotive catalytic converters. Sci Total Environ 270:165–173

Moldovan M, Gomez MM, Palacios MA (1999) Determination of platinum, rhodium and palladium in car exhaust fumes. Anal Atom Spectrom 14:1163–1169

Orecchio S (2007) PAHs associated with leaves of Quercus ilex L.: extraction, GC-MS analysis, distribution and sources. Assessment of air quality in the Palermo (Italy) area. Atmos Environ 41:8669–8680

Orecchio S (2010) Contamination from polycyclic aromatic hydrocarbons (PAHs) in the soil of a botanical garden localized next to a former manufacturing gas plant in Palermo (Italy). Hazard Mater 180:590–601

Orecchio S, Amorello D (2010) Platinum and rhodium associated with the leaves of *Nerium oleander* L.; analytical method using voltammetry; assessment of air quality in the Palermo (Italy) area. J Hazard Mater 174:720–727

Orecchio S, Amorello D (2011) Platinum levels in urban soils from Palermo (Italy); analytical method using voltammetry. Microchem J 99:283–288

Orecchio S, Amorello D, Carollo C (2012) Voltammetric determination of platinum in perfusate and blood: preliminary data on pharmacokinetic study of arterial infusion with oxaliplatin. Microchemical 100:72–76

Palacios MA, Moldovan M, Gómez M (2000) The automobile catalyst as an important source of PGE in the environment. In: Zereini F (ed) Anthropogenic platinum group element emission: their impact on man and environment. Springer, Berlin, pp 3–14

Petrucci F, Bocca B, Alimonti A, Caroli S (2000) Determination of Pd, Pt, Rh in airborne particulate and road dust by high-resolution ICP-MS: a preliminary investigation of the emission from auto motive catalysts in the urban area of Rome. Anal Atom Spectrom 15:525–535

Piech R, Basa B, Kubiaka WW (2008) The cyclic renewable mercury film silver based electrode for determination of molybdenum (VI) traces using adsorptive stripping voltammetry. Talanta 76:295–300

Rauch S, Lu M, Morrison GM (2001) Heterogeneity of platinum group metals in airborne particles. Environ Sci Technol 35:595–599

Rauch S, Hemond HF, Peucker-Ehrenbrink B, Ek KH, Morrison GM (2005) Platinum group element concentrations and osmium isotopic composition in urban airborne particles from Boston, Massachusetts. Environ Sci Technol 39:9464–9470

Rauch S, Peucker-Ehrenbrink B, Molina LT, Molina MJ, Ramos R, Hemond H (2006) Platinum group elements in airborne particles in Mexico City. Environ Sci Technol 40(75):54–60

Rubino S, Portanova P, Girasolo A, Calvaruso G, Orecchio S, Stocco GC (2009) Synthetic, structural and biochemical studies of polynuclear platinum (II) complexes with heterocyclic ligands. Europ J Med Chem 44:1041–1048

Skoog DA, Leary J (2000) Chimica analitica strumentale. Edises, Napoli

Stoica AI, Peltea M, Baiulescu GE, Ionica M (2004) Determination of cobalt in pharmaceutical products. J Pharm Biomed Anal 36:653–656

Sures B, Zimmermann S, Messerschmidt J, von Bohlen A, Alt F (2001) First report on the uptake of automobile catalyst emitted palladium by European eels (Anguilla anguilla) following experimental exposure to road dust. Environ Pollut 113:341–345

Vlasankova R, Otruba V, Bendl J, Fisera M, Kanicky V (1999) Preconcentration of platinum group metals on modified silica gel and their determination by inductively coupled plasma atomic emission spectrometry and inductively coupled plasma mass spectrometry in airborne particulates. Talanta 48:839–846

Wiseman CLS, Zereini F (2009) Airborne particulate matter, platinum group elements and human health: a review of recent evidence. Sci Total Environ 407:2493–2500

Zereini F, Alt F (eds) (2000) Anthropogenic platinum group element emission: their impact on man and environment. Springer, Berlin, pp 33–44

Zereini F, Wiseman C, Alt F, Messerschmidt J, Müller J (2001) Urban H., platinum and rhodium concentrations in airborne particulate matter in Germany from 1988 to 1998. Environ Sci Technol 35:1996–2000

Zimmermann S, Menzel CM, Berner Z, Eckhardt JD, Stuben D, Alt F, Messerschmidt J, Taraschewski H, Sures B (2001) Trace analysis of platinum in biological samples: a comparison between sector field ICP-MS and adsorptive cathodic stripping voltammetry following different digestion procedures. Anal Chim Acta 439:203–209

Speciation Analysis of Chloroplatinates

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Abstract Metallic form of platinum is considered to be inert for biological reactions, but in contrast some Pt salts like hexachloroplatinate and tetrachloroplatinate, present at processes in platinum industry and at production of cytostatic platinum compounds, are among the most potent allergens and sensitizers. To assess their potential health risk, development of selective and sensitive analytical methods is inevitable. These compounds can be also found in various environmental compartments where they are released from car catalysts. However, the levels are often orders of magnitude lower which requires effective pretreatment prior to their analysis. In the present work, the most frequently methods used for the preconcentration as well as for speciation analysis of the chlorinated platinum compounds, either in occupational environment or in various natural matrices, will be presented and discussed.

Abbreviations

CE	Capillary electrophoresis
CE-ICP-MS	Capillary electrophoresis—inductively coupled plasma mass spectrometry
HPLC	High performance liquid chromatography
ICP-MS	Inductively coupled plasma mass spectrometry
LC	Liquid chromatography
LC-ICP-MS	Liquid chromatography—inductively coupled plasma mass spectrometry
OEL	Occupational exposure limit
PGMs	Platinum group metals

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1 Introduction

Accumulation of platinum is increasing in the environment over the time. Catalytic converters of modern vehicles, in addition to its other applications (e.g. industrial, jewelry, anticancer drugs, etc.), are considered to be the main sources of Pt. The metallic form of this element is considered to be biologically inert and non-allergenic, thus the sensitizing potential is probably very low. However, there is epidemiological evidence that the sensitizing potential of Pt compounds is related to a group of charged halogenated compounds that contain reactive ligand systems, the most effective of which are chloride ligands (WHO 1991; Merget et al. 2000). A sensitization level of 0.1 $\mu g\ m^{-3}$ in air for these soluble platinum compounds was reported (Rosner and Merget 2000). The allergic response to Pt increases with increasing number of chlorine atoms, the most potent compounds being hexachloroplatinic (IV) acid and its ammonium and potassium salts, and potassium and sodium tetrachloroplatinite (II) (Schuppe et al. 1997). Following the precautionary principle, government agencies in Europe (The Health Council of the Netherlands Expert Committee on Occupational Standards—DECOS) (Joint Statement of the International Platinum Group Metals Association (IPA) and the European Precious Metals Federation (EPMF) 2008) and the United States (Environmental Protection Agency—EPA) are now asserting that the regulation of chloroplatinate sensitization in the workplace, and beyond, should be far more strict, and are proposing new occupational exposure limits (OEL) for chloroplatinates that are several orders of magnitude below current limits (Bullock 2010).

It has been shown that sensitized workers removed immediately from further contact with Pt salts showed no evidence of long-term effects (Hughes 1980). But further occupational exposure in sensitized subjects leads to persistence, and sometimes to progressive deterioration of asthma, irrespective of the reduction of exposure to the specific sensitizer. Linnett and Hughes (1999) estimated the cumulative chance of being sensitized after 5 years of chloroplatinate exposure as 51 % in a group of workers consistently exposed to chemical processes. However, increased Pt concentrations, compared to natural levels, were reported not only in human body fluids (blood, urine, etc.) and tissue of occupationally exposed persons (Merget et al. 2000), but also in body fluids of non-occupationally exposed persons (Vaughan and Florence 1992; Begerow et al. 1997; Caroli et al. 2001; Bocca et al. 2004). These findings show that platinum compounds have harmful effects on the human health by direct contact with the dust and by inhalation of airborne particulate matter (Rosner and Merget 2000) as well as by take-up of platinum via the food chain.

Besides the elevated amounts of Pt in the occupational environment, there is an evidence of spread and bioaccumulation of this metal in diverse environmental matrices as airborne particulate matter, soil, roadside dust and vegetation, river, coastal and oceanic environment (Ravindra et al. 2004; Bencs et al. 2011). Pt compounds in these matrices can be soluble; consequently, they enter the waters, sediments and soil (Colombo et al. 2008). Soil exposed to high traffic densities exceeds the natural background value of platinum group metals, and is influenced by local conditions (traffic frequency, distance from the traffic-lane, wind direction, barriers—vegetation and changes of the local environment). Hence, most of the investigations discuss samples of soil and vegetation adjacent to heavily traveled highways and of road dust swept from the roadways (Table 1). The Pt:Rh ratios were usually found about 6, close to that applied in catalytic converters. The distributions of Pt were found highly non-homogeneous, which revealed a similar distribution pattern like in airborne particles.

From the available information we can assume that the mobility and impact of platinum on human health is strongly depending on the chemical form of the metal. Various studies of the particular topic of platinum metals appeared in the literature;

Table 1 Platinum concentrations in soil and road dust

Sample	Location	Specification	Pt concentration	Reference
Roadside dust	South California	Heavy traffic	Up to 680 ng g^{-1}	Hodge and Stallard (1986)
Road dust	Göteborg	Collected 1984–1991	Particles size <63 µm: 3.0–8.9 ng g^{-1} 63–125 µm: 1.5–3.6 ng g^{-1} 125–1,000 µm: <0.5–2.8 ng g^{-1}	Wei and Morrison (1994)
Roadside soil	Germany	Near highways	Up to 253 ng g^{-1}	Cubelic et al. (1997)
Soil and road dust	Southwest Germany	Highway	Up to hundreds of ng g^{-1}	Schäfer and Puchelt (1998)
Road sediment	Göteborg	1984–1998	Up to 171 ng g^{-1}	Rauch et al. (2000)
Roadside soil and grass	USA	Adjacent to the roadside	64–73 ng g^{-1}	Ely et al. (2001)
Roadside soil	Mexico City	Dependent on the traffic conditions	Up to 333 ng g^{-1}	Morton et al. (2001)
Road dust, roadside soil	Seoul, Korea	Dependent on the traffic density	Urban road dust: 3.8–444 ng g^{-1} Urban roadside soil: 0.7–221 ng g^{-1} Suburbs road dust: 2.3–5.2 ng g^{-1} Suburbs roadside soil: 0.4–5.1 ng g^{-1}	Lee et al. (2012)
Tunnel and road dust	Houston, Texas	High-traffic roadways, busy underwater tunnel	35–131 ng g^{-1} 529 ± 130 ng g^{-1}	Spada et al. (2012)

i.e. on their distribution and speciation in environmental compartments (Hays et al. 2011; Zereini et al. 2012), the determination methods of the metals in environmental samples (Barefoot and van Loon 1999; Kanitsar et al. 2003; Standler et al. 2007; Balcerzak 2011), and the possible health risk of anthropogenic platinum metals (Rosner and Merget 2000). In the present contribution, the most frequently methods used for chlorinated platinum species determination, either in occupational environment or in various natural matrices, will be discussed.

2 Analysis of Total Platinum

First of all, total platinum analysis is necessary in order to assess the species distribution in occupational and environmental samples. Determination of platinum in atmospheric aerosols is particularly important in relation to human health because molecules of these metals can enter the human body via the respiratory tract (fraction <10 μm) (Dubiella-Jackowska et al. 2007). The detection of total platinum concentrations in environmental matrices requires very sensitive and selective instrumental methods, such as instrumental neutron activation analysis (INAA) (Probst et al. 2001), graphite furnace atomic absorption spectroscopy (GF-AAS), electrothermal atomic absorption spectrometry (ET-AAS) (Tilch et al. 2000), cathodic stripping voltammetry (CSV) (Zereini et al. 2001), inductively coupled plasma mass spectrometry (ICP-MS) (Farago et al. 1998; Hann et al. 2003; Köllensperger et al. 2003; Curtis et al. 2010), and inductively coupled plasma optical emission spectrometry (ICP-OES) (Orecchio and Amorello 2011; Van Wyk et al. 2011, 2012). Objectives of methodological work concern sample pre-treatment procedures for preconcentration and selective and quantitative separation from interfering elements. Despite the effectiveness of a large number of matrix separation methods, the application of such procedures to determine ultra-trace levels of Pt is not straightforward. Spectroscopic interferences arising from more abundant constituents of the sample, as well as the risk of contamination during sample manipulation become increasingly serious with decreasing analyte concentration, especially in complex matrices. Consequently, trace analysis of Pt in such matrices is ideally performed via matrix separation, analyte preconcentration and quantification by isotope dilution analysis with mass spectrometric detection (IDMS) (Kanitsar et al. 2003).

3 Speciation Analysis of Chloroplatinates in Environmental Matrices

As already mentioned, Pt provides an excellent example for the high significance of speciation for assessment of the toxicity of a metal and its compounds. In order to investigate the behavior of the platinum species, of which the chlorinated compounds appeared to pose the highest potential health risk, selective and sensitive analytical methods are required. ICP–MS is suitable for analysis of Pt species, because of its extremely low detection limits, multielement capabilities and wide linear dynamic range (five to six orders). However, the complexity of many environmental matrices and the need to discriminate among analytes that have very close physicochemical properties prompted the development of high-resolution separation techniques. One of these techniques is liquid chromatography (LC) with all different possibilities of chemistry of stationary phase material as well as capillary electrophoresis (CE) based on the separation in an electric field.

Nevertheless, it is noteworthy that the environmental levels of platinum species are expected to be two to four orders of magnitude lower. Therefore an effective pretreatment of such samples is necessary. Various approaches have been developed in this area so far and they will be discussed in the following chapters together with the most often used instrumental techniques used within platinum chlorides determination.

3.1 Enrichment Methods for Pre-concentration of Chlorinated Platinum Species

In the case of low abundant platinum species in environmental samples sample pretreatment different procedures for pre-concentration and selective and quantitative separation from interfering elements have been developed and applied to the determination of Pt compounds by AAS, ICP–AES and ICP–MS techniques. Generally, these procedures can be divided into five groups including precipitation and coprecipitation, liquid–liquid extraction, solid phase extraction, electrochemical pre-concentration and biosorption (Godlewska-Zylkiewicz 2004).

Solid phase extraction (SPE) offers a number of important advantages in comparison with traditional liquid-liquid extraction, such as reduced organic solvents usage and exposure, high enrichment factor, rapid phase separation and the ability of combination with different detection techniques (Chen et al. 2011; Das et al. 2012; Augusto et al. 2013). The mechanism of sorption depends on the nature of a given sorbent and may include simple adsorption, complexation or ion-exchange.

The high affinity of platinum chlorine complexes for strongly basic anion-exchange resins as well as their weak affinity for cation-exchange resins can be used for separating them from sample matrix. Ion exchange technique is very suitable for eliminating spectral interference in the determinations of platinum by ICP–MS (Godlewska-Zylkiewicz 2004). Selectivity of anion exchangers is high due to the formation of stable ion pairs between chloro complexes and the sorbent's active groups. The tendency for the metal-chloro complexes to form ion pairs with anion-exchangers is: $[MCl_6]^{2-} > [MCl_4]^{2-} >> [MCl_6]^{3-} >$ aquo species, where M is a metal (Bernardis et al. 2005), which makes it an ideal method for pre-concentration of chloro-complexes prior to speciation analysis.

Recent tendencies on the research of the separation and preconcentration of platinum metal ions are focused to novel sorbent materials (Mladenova et al. 2012). There is a growing interest in sorbents based on nanostructured materials such as magnetic nanoparticles (Zhou et al. 2010; Li et al. 2011a) and activated carbon materials (Tu et al. 2011; Li et al. 2011b). Ion imprinted polymers properties are remarkable because of their high selectivity towards the target ion due to a memory effect resulting from their preparation process (Godlewska-Żyłkiewicz et al. 2010; Leśniewska et al. 2011).

3.2 Platinum Speciation with LC–ICP–MS

Coupling of liquid chromatography with ICP–MS is straightforward. Nebulizers are available that can accept the effluent from standard, μ-HPLC (high performance liquid chromatography) and nano-HPLC. With all the different possibilities of ion-exchange, reverse-phase, affinity, size-exclusion, ion-pairing and any other of the numerous techniques, liquid chromatography offers a very rich tool-box for platinum speciation. LC–ICP–MS has important advantages for speciation analysis as complex chromatograms are reduced to simple "elementograms" and the quantification of even unknown elemental species is possible with respect to the detected element due to compound independent sensitivity without the necessity of having standards, i.e. species unspecific isotope dilution analysis (Köllensperger et al. 2003). Moreover, LC–ICP–MS is suitable for accurate ultra trace speciation analysis of platinum because of its extremely low detection limits. However, only few studies deal with the speciation of platinum at trace and ultratrace levels in these matrices. The technique has been applied for the determination of platinum compounds in environmental samples such as dust (Nischwitz et al. 2003), water (Hann et al. 2005; Dubiella-Jackowska et al. 2009; van Wyk et al. 2011, 2012; Xing et al. 2013), and plant and soil extracts (Klueppel et al. 1998; Lustig et al. 1998, respectively). Nachtigall et al. (1997) established an ion chromatographic method for the speciation of chloroplatinates in road dust. This method was used by Nischwitz et al. (2003) in combination with ICP–MS detection. The main drawback of this method was the oxidizing conditions in the mobile phase, which in combination with the long analysis time, compromised method accuracy. Zoorob et al. (1998) short column lifetimes and reproducibility problems as a disadvantage of the technique. Additionally, problems associated with organic solvents (i.e. signal suppression and low long-term stability) remained the same as those with conventional RPLC (reversed-phase liquid chromatography). Nevertheless, the hyphenated system resulting from the coupling of LC and ICP–MS is the most often used system for speciation analysis related to the ICP–MS detection.

3.3 Platinum Speciation with CE-ICP-MS

The complexity of many environmental and biological matrices and the need to discriminate among analytes that have very close physicochemical properties prompted the development of high-resolution separation techniques prior to sensitive element- or molecule-specific detection. One of these techniques based on the separation in an electric field is capillary electrophoresis (CE). CE has certain advantages in comparison to chromatographic techniques, such as unique selectivity enabling the separation of cationic, anionic and neutral compounds within one run, and high separation efficiency with theoretical plate numbers ranging from 70,000 to 200,000. The mechanism of separation of metal ions in CE is based on the difference in electrophoretic mobility of the metal ions. While CE supplements conventional HPLC methods, it shows unique promise for separation purpose because it causes only a minor disturbance to the existing equilibrium between different species. There is no stationary phase, which has a huge surface area and gives various possibilities for undesired interactions. Therefore, species transformations are thought to be less frequent than with HPLC (Timerbaev et al. 2002).

To achieve maximum separation by CE, optimization of CE parameters is critical. The independent parameters under the control of the analysts are: selection of the buffer (its pH and ion strength), applied voltage, temperature and dimensions of the capillary, and additives to the background electrolyte. CE–ICP–MS can be used for speciation studies of chloroplatinates. As key advantage, the method offers moderate analysis time together with high separation efficiency. Moreover, the use of oxidizing buffers can be easily avoided. The CE was interfaced by a functional make-up flow design using a micro concentric nebulizer (Standler et al. 2007). In elemental speciation the high precision of migration times is mandatory for unambiguous identification of the detected species. Standler et al. (2007) studied and compared different quantification strategies in terms of their total combined uncertainty. Species-specific external calibration with and without internal standardization was compared to species-specific quantification by isotope dilution mass spectrometry for the determination of platinum species concentration demonstrating the potential of this method for platinum speciation.

Other authors used this hyphenated technique for successful Pt speciation. After the method optimization, electropherograms with high resolution were obtained, showing low detection limits around 1 μg L^{-1} and very high resolution (Michalke and Schramel 1997). Lustig et al. (1998) used this technique for aqueous extracts of a clay-like humic soil, treated with a Pt contaminated tunnel dust and Pt model compounds for examination of transformation processes of Pt-species in a soil.

3.4 Platinum Speciation with Adsorptive Voltammetry

Platinum metals species are also determinable via electrochemical principles. In this respect, electrochemical stripping analysis is especially suitable, offering a high analytical performance at relatively low expenses. The respective procedures usually involve the catalytic effect making such measurements extremely sensitive (Bobrowski and Zarębski 2000). This is also the case of classical formazone method, being able of achieving down to 1×10^{-13}M Pt(IV), thus allowing one to determine platinum in sea water at the base level (Kowalska et al. 2004). Švancara et al. (2007) applied a carbon pase electrode modified in situ with cationic surfactants for the determination of platinum metals via suitable complex ions. Adsorptive differential pulse stripping voltammetric measurements for Pt(II) were performed in freshwater and sediment samples in the presence of dimethylglyoxime as complexing agent (van der Horst et al. 2012). The glassy carbon bismuth film electrode (GC/BiFE) exhibited good and reproducible sensor characteristics.

4 Conclusion

Chlorinated platinum salts possess the highest sensitizing potential amongst all Pt species, therefore their proper determination is of great importance in respect to the health protection. Determination of these Pt species in environmental and occupational samples is highly challenging. First, due to the high concentration of interfering matrix components and second, due to the low content of these compounds, especially in various environmental matrices (dust, water, soil). High selectivity and sensitivity can be achieved by combination of an effective preconcentration/separation procedures followed by appropriate instrumental technique. Liquid chromatography or capillary electrophoresis hyphenated with inductively coupled plasma mass spectrometry appear to be the most effective approaches with respect to achieving the trace levels of chlorinated Pt species either in occupational or natural environment.

References

Augusto F, Hantao LW, Mogollón GS, Braga SCG (2013) New materials and trends in sorbents for solid-phase extraction. Trends Anal Chem 43:14–23

Balcerzak M (2011) Methods for the determination of platinum group elements in environmental and biological materials: a review. Crit Rev Anal Chem 41:214–235

Barefoot RR, Van Loon JC (1999) Recent advances in the determination of the platinum group elements and gold. Talanta 49:1–14

Begerow J, Turfeld M, Dunemann L (1997) Determination of physiological palladium and platinum levels in urine using double focusing sector field ICP-MS. Fresenius J Anal Chem 359:427–429

Bencs L, Ravindra K, Van Grieken R (2011) Platinum: environmental pollution and health effects. In: Enc environment health, pp 580–595

Bernardis FL, Grant RA, Sherrington DC (2005) A review of methods of separation of the platinum-group metals through their chloro-complexes. React Funct Polym 65:205–217

Bobrowski A, Zarębski J (2000) Catalytic systems in adsorptive stripping voltammetry. Electroanalysis 12:1177–1186

Bocca B, Alimonti A, Cristaudo A, Cristallini E, Petrucci F, Caroli S (2004) Monitoring of the exposure to platinum-group elements for two Italian population groups through urine analysis. Anal Chim Acta 512:19–25

Bullock J (2010) Chloroplatinate toxicity: use and misunderstanding of Merget. International Precious Metals Institute, Pensacola

Caroli S, Alimonti A, Petrucci F, Bocca B, Krachler M, Forastiere F, Sacerdote MT, Mallone S (2001) Assessment of exposure to platinum-group metals in urban children. Spectrochim Acta B 56:1241–1248

Chen L, Wang T, Tong J (2011) Application of derivatized magnetic materials to the separation and the preconcentration of pollutants in water samples. Trends Anal Chem 30:1095–1108

Colombo C, Oates CJ, Monhemius AJ, Plant JA (2008) Complexation of platinum, palladium and rhodium with inorganic ligands in the environment. Geochem: Explor Env A 8:91–101

Cubelic M, Pecoroni R, Schäfer J, Eckhardt JD, Berner Z, Stüben D (1997) Verteilung verhkersbedingter Edelemetallimmissionen in Böden. Umweltwissenschaften und Schadstoff-Forschung—Untertitel Zeitschrift für Umweltchemie und Ökotoxikologie (in German) 9:249–258

Curtis L, Turner A, Vyas N, Sewell G (2010) Speciation and reactivity of cisplatin in river water and seawater. Environ Sci Technol 44:3345–3350

Das D, Gupta U, Das AK (2012) Recent developments in solid phase extraction in elemental speciation of environmental samples with special reference to aqueous solutions. Trends Anal Chem 33:35–45

Dubiella-Jackowska A, Polkowska Z, Namieśnik J (2007) Platinum group elements: A challenge for environmental analytics. Pol J Environ Stud 16:329–345

Dubiella-Jackowska A, Polkowska Z, Dariusz L, Pasławski P, Staszek W, Namieśnik J (2009) Estimation of platinum in environmental water samples with solid phase extraction technique using inductively coupled plasma mass spectrometry. Cent Eur J Chem 7:35–41

Ely JC, Neal CR, Kulpa CF, Schneegurt MA, Seidler JA, Jain JC (2001) Implications of platinum-group element accumulation along US roads from catalytic-converter attrition. Environ Sci Technol 35:3816–3822

Farago ME, Kavanagh P, Blanks R, Kelly J, Kazantzis G, Thornton I, Simpson PR, Cook JM, Delves HT, Hall GE (1998) Platinum concentrations in urban road dust and soil, and in blood and urine in the United Kingdom. Analyst 123:451–454

Godlewska-Żyłkiewicz B (2004) Preconcentration and separation procedures for the spectrochemical determination of platinum and palladium. Microchim Acta 147:189–210

Godlewska-Żyłkiewicz B, Leśniewska B, Wawreniuk I (2010) Assessment of ion imprinted polymers based on Pd(II) chelate complex for preconcentration and FAAS determination of palladium. Talanta 83:596–604

Hann S, Köllensperger G, Kanitsar K, Stingeder G, Brunner M, Erovic B, Müller M, Reiter C (2003) Platinum determination by ICP-SFMS in different matrices relevant for human biomonitoring. Anal Bioanal Chem 376:198–204

Hann S, Stefánka Z, Lenz K, Stingeder G (2005) Novel separation method for highly sensitive speciation of cancerostatic platinum compounds by HPLC-ICP-MS. Anal Bioanal Chem 381:405–412

Hays MD, Cho S-H, Baldauf R, Schauer JJ, Shafer M (2011) Particle size distributions of metal and non-metal elements in an urban near-highway environment. Atmos Environ 45:925–934

Hodge VF, Stallard MO (1986) Platinum and palladium in roadside dust. Environ Sci Technol 20:1058–1060

Hughes EG (1980) Medical surveillance of platinum refinery workers. J Soc Occup Med 30:27–30

Joint Statement of the International Platinum Group Metals Association (IPA) and the European Precious Metals Federation (EPMF) on the DECOS recommendation for a revised health-based occupational exposure limit applicable to chloroplatinates (2008)

Kanitsar K, Köllensperger G, Hann S, Limbeck A, Puxbaum H, Stingeder G (2003) Determination of Pt, Pd and Rh by inductively coupled plasma sector field mass spectrometry (ICP–SFMS) in size-classified urban aerosol samples. J Anal At Spectrom 18:239–246

Köllensperger G, Hann S, Nurmi J, Prohaska T, Stingeder G (2003) Uncertainty of species unspecific quantification strategies in hyphenated ICP-MS analysis. J Anal At Spectrom 18:1047–1055

Kowalska J, Huszal S, Sawicki MG, Asztemborska M, Stryjewska E, Szalacha E, Golimowski J, Gawronski SW (2004) Voltammetric determination of platinum in plant material. Electroanalysis 16:1266–1270

Klueppel K, Jakubowski N, Messerschmidt J, Stuewer D, Klockow D (1998) Speciation of platinum metabolites in plants by size-exclusion chromatography and inductively coupled plasma mass spectrometry. J Anal At Spectrom 13:255–262

Lee HY, Chon HT, Sager M, Marton L (2012) Platinum pollution in road dusts, roadside soils, and tree barks in Seoul, Korea. Environ Geochem Health 34:5–12

Leśniewska B, Kosińska M, Godlewska-Żyłkiewicz B, Zambrzycka E, Wilczewska AZ (2011) Selective solid phase extraction of platinum on an ion imprinted polymers for its electrothermal atomic absorption spectrometric determination in environment al samples. Microchim Acta 175:273–282

Li Y, Huang YF, Jiang Y, Tian BL, Han F, Yan XP (2011a) Displacement solid-phase extraction on mercapto-functionalized magnetite microspheres for inductively coupled plasma mass spectrometric determination of trace noble metals. Anal Chim Acta 692:42–49

Li D, Chang X, Hu Z, Wang Q, Tu Z, Li R (2011b) Selective solid-phase extraction of Au(III), Pd (II) and Pt(IV) using activated carbon modified with 2,6-diaminopyridine. Microchim Acta 174:131–136

Linnett PJ, Hughes EG (1999) 20 years of medical surveillance on exposure to allergenic and non-allergenic platinum compounds: the importance of chemical speciation. Occup Environ Med 56:191–196

Lustig S, Michalke B, Beck W, Schramel P (1998) Platinum speciation with hyphenated techniques: high performance liquid chromatography and capillary electrophoresis on-line coupled to an inductively coupled plasma mass spectrometer—application to aqueous extracts from a platinum treated soil. Fresenius J Anal Chem 360:18–25

Merget R, Kulzer R, Dierkes-Globisch A (2000) Exposure-effect relationship of platinum salt allergy in a catalyst production plant: conclusions from a 5-year prospective cohort study. J Allergy Clin Immunol 105:364–370

Michalke B, Schramel P (1997) Coupling of capillary electrophoresis with ICP-MS for speciation investigations. Fresenius J Anal Chem 357:594–599

Mladenova E, Karadjova I, Tsalev DL (2012) Solid-phase extraction in the determination of gold, palladium, and platinum. J Sep Sci 35:1249–1265

Morton O, Puchelt H, Hernández E, Lounejeva E (2001) Traffic-related platinum group elements (PGE) in soils from Mexico City. J Geochem Explor 72:223–227

Nachtigall D, Artelt S, Wünsch GJ (1997) Speciation of platinum–chloro complexes and their hydrolysis products by ion chromatography: Determination of platinum oxidation states. J Chromatogr A 775:197–210

Nischwitz V, Michalke B, Kettrup A (2003) Speciation of Pt(II) and Pt(IV) in spiked extracts from road dust using on-line liquid chromatography-inductively coupled plasma mass spectrometry. J Chromatogr A 1016:223–234

Orecchio S, Amorello D (2011) Platinum levels in urban soils from Palermo (Italy); Analytical method using voltammetry. Microchem J 99:283–288

Probst T, Rietz B, Alfassi ZB (2001) Platinum concentrations in Danish air samples determined by instrumental neutron activation analysis. J Environ Monit 3:217–219

Rauch S, Motelica-Heino M, Morrison GM, Donard OFX (2000) Critical assessment of platinum group element determination in road and urban river sediments using ultrasonic nebulization and high resolution ICP-MS. J Anal At Spectrom 15:329–334

Ravindra K, Bencs L, Van Grieken R (2004) Platinum group elements in the environment and their health risk. Sci Total Environ 318:1–43

Rosner G, Merget R (2000) Evaluation of the health risk of platinum emissions from automotive emission control catalyts. In: Zereini F, Alt F (eds) Anthropogenic platinum group element emissions. Their impact on man and environment. Springer, Berlin, pp 267–284

Schäfer J, Puchelt H (1998) Platinum-Group-Metals (PGM) emitted from automobile catalytic converters and their distribution in roadside soils. J Geochem Explor 64:307–314

Schuppe HC, Kulig J, Lerchenmüller C, Becker D, Gleichmann E, Kind P (1997) Contact hypersensitivity to disodium hexachloroplatinate in mice. Toxic Lett 93:125–133

Spada N, Bozlaker A, Chellam S (2012) Multi-elemental characterization of tunnel and road dusts in Houston, Texas using dynamic reaction cell-quadrupole-inductively coupled plasma–mass spectrometry: evidence for the release of platinum group and anthropogenic metals from motor vehicles. Anal Chim Acta 735:1–8

Standler A, Köllensperger G, Buchberger W, Stingeder G, Hann S (2007) Determination of chloroplatinates by CE coupled to inductively coupled plasma sector field MS. Electrophoresis 28:3492–3499

Švancara I, Galík M, Vytřas K (2007) Stripping voltammetric determination of platinum metals at a carbon paste electrode modified with cationic surfactants. Talanta 72:512–518

Tilch J, Schuster M, Schwarzer M (2000) Determination of palladium in airborne particulate matter in a German city. Fresenius J Anal Chem 367:450–453

Timerbaev AR, Küng A, Keppler BK (2002) Capillary electrophoresis of platinum-group elements: analytical, speciation and biochemical studies. J Chromatogr A 945:25–44

Tu Z, Lu S, Chang X, Li Z, Hu Z, Zhang L, Tian H (2011) Selective solid-phase extraction and separation of trace gold, palladium and platinum using activated carbon modified with ethyl-3-(2-aminoethylamino)-2-chlorobut-2-enoate. Microchim Acta 173:231–239

Van der Horst C, Silwana B, Iwuoha E, Somerset V (2012) Stripping voltammetric determination of palladium, platinum and rhodium in freshwater and sediment samples from South African water resources. J Environ Sci Health 47:2084–2093

Vaughan GT, Florence TM (1992) Platinum in the human diet, blood, hair and excreta. Sci Total Environ 111:47–58

Van Wyk PH, Gerber WJ, Koch KR (2011) A robust method for speciation, separation and photometric characterization of all $[PtCl_{6-n}Br_n]^{2-}$ (n = 0–6) and $[PtCl_{4-n}Br_n]^{2-}$ (n = 0–4) complex anions by means of ion-pairing RP-HPLC coupled to ICP-MS/OES, validated by high resolution ^{195}Pt NMR spectroscopy. Anal Chim Acta 704:154–161

Van Wyk PH, Gerber WJ, Koch KR (2012) Direct determination of metal to halide mole ratios in platinum complex anions $[PtCl_{6-n}Br_n]^{2-}$ (n = 0–6) by means of HPLC-ICP-OES using Cl, Br and Pt emissions of all separated species. J Anal At Spectrom 27:577–580

Wei C, Morrison GM (1994) Platinum in road dusts and urban river sediments. Sci Total Environ 146(147):169–174

WHO (1991) Environmental health criteria 125—platinum. World Health Organization, International Programme on Chemical Safety, Geneva

Xing L, Jerkiewicz G, Beauchemin D (2013) Ion exchange chromatography coupled to inductively coupled plasma mass spectrometry for the study of Pt electro-dissolution. Anal Chim Acta 785:16–21

Zereini F, Wiseman C, Alt F, Messerschmidt J, Müller J, Urban H (2001) Platinum and rhodium concentrations in airborne particulate matter in Germany from 1988 to 1998. Environ Sci Technol 35:1996–2000

Zereini F, Alsenz H, Wiseman CLS, Püttmann W, Reimer E, Schleyer R, Bieber E, Wallasch M (2012) Platinum group elements (Pt, Pd, Rh) in airborne particulate matter in rural versus. urban areas of Germany: concentrations and spatial patterns of distribution. Sci Total Environ 416:261–268

Zhou L, Xu J, Liang X, Liu Z (2010) Adsorption of platinum(IV) and palladium(II) from aqueous solution by magnetic cross-linking chitosan particles modified with ethylenediamine. J Hazard Mater 182:518–524

Zoorob GK, McKiernan JW, Caruso JA (1998) ICP-MS for elemental speciation studies. Microchim Acta 128:145–168

Analysis of Platinum Group Elements in Environmental Samples: A Review

Roland Schindl and Kerstin Leopold

Abstract This review critically discusses techniques for separation, pre-concentration and detection of platinum group elements in environmental samples. State-of-the-art methods and novel approaches, which were published after 2005 are described and summarized. Thereby, only publications were considered where measurements of real environmental samples and/or reference materials were performed for proof of applicability.

1 Introduction

The natural occurrence of platinum group elements (PGEs) in the upper earth crust is typically in the sub µg kg^{-1} range and is limited to distinct sites where PGEs are part of noble metal-rich ores (Ru: 0.1 µg kg^{-1}; Rh: 0.06 µg kg^{-1}; Pd: 0.4 µg kg^{-1}; Os and Ir: 0.05 µg kg^{-1} and Pt: 0.4 µg kg^{-1}) (Wedepohl 1995). Their main sources of anthropogenic release into the environment are automotive catalytic converters, clinical wastewaters, jewelry industry, sewage plants, and chemical industry (Matthey 2012). As shown in Fig. 1, PGEs are emitted from these sources into waters, soils, and the atmosphere, from where they can enter plants, animals, and humans. In order to assess possible risks arising from anthropogenic PGEs emission, like for instance long-term health effects, their concentration has to be monitored in all environmental compartments, and their accumulation in plants, animals, and humans should be studied. Therefore, several analytical methodologies for reliable quantification of PGEs in these matrices at trace concentrations have been developed within the last decades and will be discussed in this review. In most studies road dust and roadside soils are studied, followed by water and plant samples. Moreover, among the PGEs mainly platinum (Pt), palladium (Pd), and

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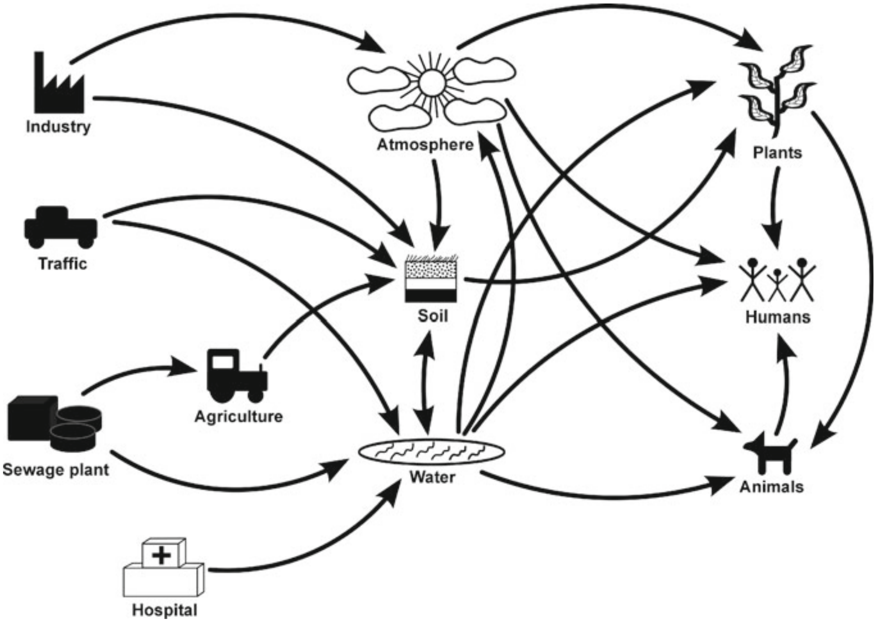
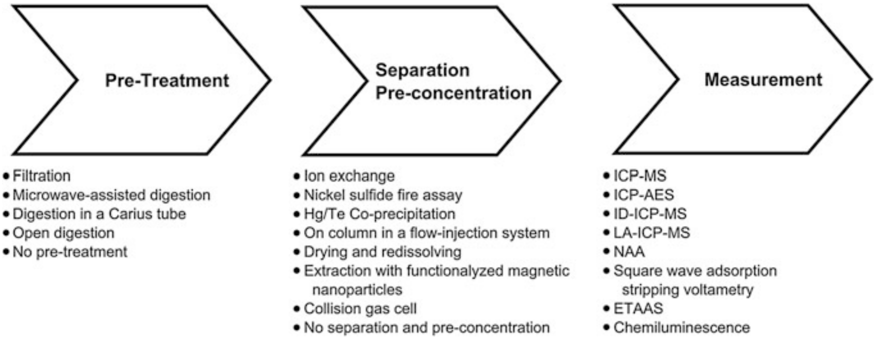


Fig. 1 Main emission sources and distribution pathways of platinum group elements in the environment



- Filtration
- Microwave-assisted digestion
- Digestion in a Carius tube
- Open digestion
- No pre-treatment

- Ion exchange
- Nickel sulfide fire assay
- Hg/Te Co-precipitation
- On column in a flow-injection system
- Drying and redissolving
- Extraction with functionalyzed magnetic nanoparticles
- Collision gas cell
- No separation and pre-concentration

- ICP-MS
- ICP-AES
- ID-ICP-MS
- LA-ICP-MS
- NAA
- Square wave adsorption stripping voltametry
- ETAAS
- Chemiluminescence

Fig. 2 Principle analytical procedure for PGE determination in environmental samples and examples for applied techniques

rhodium (Rh) are determined, because they are more often applied than the other three PGEs, iridium (Ir), ruthenium (Ru), and osmium (Os). Figure 2 displays an overview on the general analytical procedure for PGE analysis in environmental samples. All analytical steps are discussed in the following and examples for new developments and novel approaches are detailed. Table 1 summarizes the concentration ranges of Pt, Pd, and Rh in the different environmental matrices. As can be seen, highest concentrations are detected for Pt, followed by Pd and Rh. This

Table 1 Typical concentration ranges of platinum, palladium and rhodium in different environmental matrices

	Pt	Pd	Rh	Ref.
Soil and sediments	0.1–506 μg kg^{-1}	0.41–193 μg kg^{-1}	0.08–64.1 μg kg^{-1}	Whiteley and Murray (2005), Locatelli (2006b), Wichmann et al. (2007), Zereini et al. (2007), Sutherland et al. (2007), Tsogas et al. (2008), Pan et al. (2009, Orecchio and Amorello (2011, Mihaljevič et al. (2013)
Dusts	0.4–529 μg kg^{-1}	4.5–770 μg kg^{-1}	0.1–152 μg kg^{-1}	Leśniewska et al. (2006), Limbeck (2006), Tsogas et al. (2008), Leopold et al. (2008), Malejko et al. (2010), Gao et al. (2012), Malejko et al. (2012), Spada et al. (2012), Afzali et al. (2012)
Rocks	0.14–10340 μg kg^{-1}	0.07–5420 μg kg^{-1}	0.01–850 μg kg^{-1}	Ma et al. (2013), Osbahr et al. (2013)
Sewage sludge	N/A	69–405 μg kg^{-1}	N/A	Leopold et al. (2008)
Marine biota	5–847 μg kg^{-1}	12–665 μg kg^{-1}	0.3–145 μg kg^{-1}	Essumang et al. (2010), Essumang (2010)
Air particulate matter	0.1–159 pg m^{-3}	0.06–683 pg m^{-3}	0.1–31.6 pg m^{-3}	Wichmann et al. (2007, Pan et al. (2009), Alsenz et al. (2009), Zereini et al. (2012), Puls et al. (2012)
Surface waters	0.150–0.177 μg L^{-1}	0.195 μg L^{-1}	N/A	Locatelli (2006b)
Waste water	N/A	1.82–3.16 μg L^{-1}	N/A	Afzali et al. (2012)

reflects the amounts of usage of the three elements for catalytic processes, such as in automotive catalytic converters (Matthey 2012). Traffic emissions are the main source for PGEs and therefore one observes the highest amounts in road dust. From there the PGEs are than transported via air and water, accumulate in soils and enter biota.

2 Sampling

The risk of contamination during collection and storage of environmental samples is relatively low, because PGEs are not ubiquitous. Solid samples, such as rock or soil, are collected with plastic equipment and stored after drying in polypropylene vessels (Whiteley and Murray 2005; Wichmann et al. 2007; Tsogas et al. 2008). Liquid samples, like surface waters or waste waters, are typically filtered through membrane filters and acidified after sampling in order to keep the PGEs in solution and prevent adsorption onto vessel walls. For storage polypropylene or polyethylene vessels are feasible (Locatelli 2006a).

3 Sample Pretreatment, Separation, and Pre-concentration

As detailed below most available detection techniques do not allow direct measurement of solid samples or detection of PGE traces in digests of the samples, because of either insufficient detection limits or several interferences. Hence, interference-free, sensitive detection of PGEs requires typically separation and pre-concentration of the analytes from the complex environmental matrices. For this purpose, there is a wide range of methods available, depending on the nature of the sample (liquid or solid), the matrix complicity, and the elements of interest. In this regard, separation of Pd traces from complex matrices is necessary, because the most sensitive detection technique (ICP-MS) suffers from strong interferences of abundant elements, whereas pre-concentration of Rh is important due to its extremely low concentrations in real samples.

For solid samples, especially geological samples, nickel sulfide fire assay method is well established for separation and pre-concentration of PGEs (Zereini et al. 1994). Here, from 10 to 50 g of the solid sample are mixed with nickel powder, sulfur, sodium carbonate, sodium tetra borate, calcium fluoride, and quartz sand and heated to approximately 1,000 °C in a fire clay crucible. After cooling, the crucible is broken and the nickel sulfide button is dissolved in hot hydrochloric acid. The remaining PGE particles are separated by filtration. The PGE particles are then dissolved in a mixture of hydrochloric acid and hydrogen peroxide. For further pre-concentration the solution can be evaporated and the residue is redissolved in hydrochloric acid (Wichmann et al. 2007; Zereini et al. 2007; Pan et al. 2009; Mihaljevič et al. 2013). As described this procedures requires several manually performed steps and involves high amounts of reagents and sample. Hence, very clean working conditions and accurate performance are required in order to minimize analyte loss and contamination.

For samples with extremely low PGE content and/or low available sample amounts preferably wet digestion is performed in order to transfer the analytes into an aqueous phase, decompose natural organic matter (NOM) and, in some cases, dissolute sparely soluble matrix compounds, such as silica. Especially, for analysis of Pd traces the later is important, since Pd(II) ions tend to bind strongly onto silica residues, even in highly acidic solutions. Hence, silica residues in the digests can lead to highly inconsistent results, as reported by various investigators (Totland et al. 1995; Borisov et al. 1997). Suitable wet digestion procedures for silica-containing matrices therefore include the use of hydrofluoric acid, as described e.g. by Boch et al. (2002).

Separation of PGEs from liquid samples or digests can be performed by either selective pre-concentration of PGEs or elimination of interfering matrix components. Regarding the later, application of cation exchange resin is a popular tool to eliminate interfering elements from liquid samples. Here, the affinity of PGEs for forming anion complexes is used for separation from other metal cations (Ely et al. 1999). One advantage of this simple approach is its suitability for all PGEs, however, no pre-concentration of the analytes is included. Therefore, it has been suggested to dry the eluates after cation exchange and redissolve PGEs (Shinotsuka and Suzuki 2007; Spada et al. 2012; Puls et al. 2012). Another recently published ion exchange method uses aluminum oxide powder as an anion exchange resin in order to separate and pre-concentrate negatively charged chloro complexes of PGEs (Herincs et al. 2013). This method was set up in an automated flow injection analysis system and coupled to inductively coupled plasma—atomic emission spectrometry (ICP-AES) for detection of PGEs in the eluates. However, simultaneous detection is not possible since different reagents have to be applied for elution of the individual PGE.

Highly efficient separation and pre-concentration of PGEs from liquid samples can also be achieved by tellurium (Te) or mercury (Hg) co-precipitation, first described by Messerschmidt et al. (2000) for palladium and further developed for application to other PGEs by Gómez et al. (2003). The digested sample is mixed with a mercury solution, then a formic acid solution is added and the solution is heated to simultaneously reduce mercury and palladium to their elemental state. Finally, a single droplet of mercury, containing the palladium is obtained. For analysis mercury is then evaporated. Of course, this step is disadvantageous regarding health and environmental concerns. The Te co-precipitation is performed analogously, however tin(II) chloride is used for reduction. The Te drop is then dissolved in concentrated nitric acid. After drying the residue is dissolved in aqua regia. This method can be combined e.g. with isotope dilution—inductive coupled plasma-mass spectrometry (ID-ICP-MS) for detection of Pt and Pd, providing an extremely sensitive and interference-free determination method. Other PGEs are quantified by using an external calibration (Gómez et al. 2003; Alsenz et al. 2009; Zereini et al. 2012; Ma et al. 2013).

Another approach for separation and pre-concentration of palladium ions is the use of pyridine functionalized magnetic iron oxide nanoparticles, which has been described recently by Bagheri et al. (2012). Here, the pH of the liquid sample is adjusted; functionalized iron oxide nanoparticles are added and after a defined incubation time collected with a strong permanent magnet. The concentrate is then washed with a thiourea solution and after decanting the washing solution measured by flame atomic absorption spectrometry (FAAS). The amount of sample used for this method varies from 50 to 800 mL with pre-concentration factors of up to 196. However, in combination with FAAS the method is with a detection limit of 0.15 mg L^{-1} not very sensitive. Hence, it is suitable for highly contaminated liquid samples, where large sample amounts are available.

Moreover, magnetic separation and co-precipitation by Hg or Te are performed manually and accordingly the investigation of large sample series is elaborative and time-consuming. In contrast, on-column pre-concentration methods are easier to handle and provide the opportunity to automate the procedure in a flow injection analysis system (FIAS). Such an automated on-column pre-concentration approach using modified multi-walled carbon nanotubes in a FIAS has recently been reported for Rh (Ghaseminezhad et al. 2009) and Pd separation (Afzali et al. 2012). Here, a column is packed with the modified multi-walled carbon nanotubes then the buffered sample solution is lead over the column. After washing with deionized water Rh/Pd is eluted by thiourea solution and detected by FAAS. The sample volume can be varied from 50 to 600 mL, with pre-concentration factors up to 200, using 3 mL of thiourea for elution. One disadvantage of this method is the short lifetime of the filled columns, which are only re-usable for 30 cycles. Moreover, high sample volumes are required to achieve useful pre-concentration factors, because elution volumes of several milliliters are needed. Coupling of this flow injection method to FAAS leads to a detection limit of 0.3 μg L^{-1}. Hence, for investigation of samples at environmental levels coupling to more sensitive detection technique or higher pre-concentration factors are required. For Pd trace analysis a sensitive FIA procedure has been described by Schuster and Schwarzer 1996) and was further developed and validated by application of certified reference material *Road Dust BCR-723* by Leopold et al. (2008). Here, a reversed phase material (RP-18) packed into a micro-column is loaded with a selective ligand (*N*,*N*-diethyl-*N*'-benzoyl thiourea, DEBT) and Pd is collected by complexation. Detection of Pd in the 20-μL-eluates can be performed by several techniques e.g. by electro thermal atomic absorption spectrometry (ETAAS). Thereby, sensitivity enhancements factors as high as 200 can be achieved depending on the applied sample volume which can be varied from a few mL up to 100 mL. A detection limit of 0.016 μg L^{-1} is achieved with a sample volume of approximately 3 mL and coupling of the FIAS to ETAAS.

4 Detection Techniques

There are several instrumental detection techniques available for PGE analysis, like inductively coupled plasma-atomic emission spectrometry or-mass spectrometer (ICP-AES /ICP-MS), flame or electro thermal atomic absorption spectrometry (FAAS /ETAAS), or voltammetry. As mentioned above, because of the low concentrations of PGEs in environmental samples (see Table 1) and occurring interferences from abundant elements, typically pre-concentration and/or elimination of interferences is performed prior to detection by instrumental techniques.

4.1 Inductively Coupled-Plasma Mass Spectrometry

The use of ICP-MS is undoubtedly the most popular technique in trace metal analysis due to its high sensitivity. However, in case of PGE trace analysis one has to ensure that PGEs are efficiently separated from environmental matrices before measurement, since even high resolution mass spectrometers cannot resolve all frequently occurring mass interferences (Köllensperger et al. 2000). In some cases, especially for Pd trace analysis, even application of mathematical corrections does not always lead to reliable data (Gomez et al. 2000). For palladium there are six stable isotopes, with ^{106}Pd having highest natural occurrence of 27.33 %. Some examples for the most frequent mass interferences for Pd in environmental samples are ^{88}Sr^{16}O for ^{104}Pd, ^{89}Y^{16}O for ^{105}Pd, ^{90}Zr^{16}O for ^{106}Pd, ^{92}Zr^{16}O for ^{108}Pd. Due to the ubiquitous occurrence of strontium (Sr), zirconium (Zr), and yttrium (Y) these interferences have to be considered when investigating environmental samples (Shinotsuka and Suzuki 2007; Alsenz et al. 2009). For Pt the most common mass interferences result from Hafnium-Oxygen species, like ^{178}Hf^{16}O, ^{179}Hf^{16}O, ^{180}Hf^{16}O or ^{181}Hf^{16}O interfering with ^{194}Pt, ^{195}Pt, ^{196}Pt, respectively. These interferences can be reduced e.g. by solvent extraction using *N*-benzoyl-*N*-phenylhydroxylamine in chloroform (Shinotsuka and Suzuki 2007) or by application of a collision/reaction cell (Simpson et al. 2001; Alsenz et al. 2009). Moreover, two more platinum isotopes, ^{192}Pt and ^{198}Pt, are detectable that are less interfered. For Rh detection by ICP-MS the only isotope ^{103}Rh can be observed and therefore in principle higher sensitivity should be expected. At the same time, it is not possible to select another isotope to overcome interferences like ^{63}Cu^{40}Ar. In conclusion, depending on the composition of the matrix and the PGEs of interest either highly selective separation of the analytes or application of collision/reaction cell technique must be applied in order to obtain reliable values for PGE analysis by ICP-MS.

Application of isotope dilution in ICP-MS offers the opportunity of internal correction and can provide lower detection limits due to better S/N ratios. An example for this approach has been recently published by Puls et al. (2012) for Pd and Pt determination by ID-ICP-MS in airborne particulate matter. Here, isotope spike solutions were added after total microwave-assisted digestion and a manually performed separation of interferences by cation exchange followed prior to analysis. The procedure has been validated by investigation of the standard reference material *Road Dust BCR-723*. The achieved detection limits are 0.93 pg m^{-3} for Pd and 0.50 pg m^{-3} for Pt. Alternatively, Te co-precipitation for Pt detection (Zereini et al. 2012) and Hg co-precipitated for Pd (Alsenz et al. 2009; Zereini et al. 2012) were described in combination with ID-ICP-MS determination in airborne particulate matter.

A direct method for PGE quantification in solid samples is laser ablation ICP-MS. Well homogenized solid rock samples can successfully be analyzed as shown by Gilbert et al. (2013) and Osbahr et al. (2013). The detection limits for LA-ICP-MS are in the low μg kg^{-1} range, i.e. 2.0 μg Pd kg^{-1}, 0.60 μg Pt kg^{-1} and 0.49 μg Rh kg^{-1}. For calibration suitable solid standards, like NiS-3 can be applied. The accuracy of LA-ICP-MS detection of course correlates with the grade of homogeneity of the solid sample.

4.2 Inductively Coupled Plasma- Atomic Emission Spectrometry

For PGE analysis by ICP-AES efficient pre-concentration methods have to be applied in order to achieve the required sensitivity for investigation of environmental samples (see Table 1), however less selective methods in comparison to ICP-MS are sufficient, since less interferences occur. The main interferences for Pd detection at a wavelength of 340.46 nm (most sensitive line) are iron ($\lambda = 340.44$ nm), vanadium ($\lambda = 340.44$ nm), titanium ($\lambda = 340.50$ nm) and wolfram ($\lambda = 340.53$ nm) (Winge et al. 1993). In a recently published work, a simple FIAS procedure for enrichment of Pd, Pt, and Rh on an aluminium oxide micro column coupled to ICP-AES providing detection limits in the low to sub μg kg^{-1} range (Pd: 0.7 μg L^{-1}, Pt: 2.1 μg L^{-1}, Rh: 0.3 μg L^{-1}) is described (Herincs et al. 2013). Applicability of the procedure was shown by investigation of spiked soil extracts in a concentration range of 2–5000 μg L^{-1}. However, feasibility of the procedure for investigation of non-spiked real samples has not yet been proved.

4.3 Flame Atomic Absorption Spectrometry

Determination of PGEs in environmental samples by FAAS, which provides similar sensitivity as ICP-AES, requires highly efficient pre-concentration and separation from abundant elements. Moreover, with a typical sample flow rate of ca. 2 mL min^{-1} sufficient sample volume is required for replicate measurements. A suitable pre-concentration procedure on basis of modified carbon nanotubes for determination of

Pd with FAAS providing a detection limit of 0.3 µg L^{-1} has been described above (Afzali et al. 2012). Interferences were tested by investigation of a spiked sample solution and tolerable maximum concentrations of interfering elements, like manganese, copper, zinc, and nickel were found to be 60 mg Mn L^{-1}, 15 mg Cu L^{-1}, and 8.3 mg Zn/Ni L^{-1}. The method was applied for determination of Pd in road dusts from Kerman province (Iran) after digestion with aqua regia and hydrogen peroxide, however, it has not been validated by any reference measurements.

4.4 Electro Thermal Atomic Absorption Spectrometry

In principle, ETAAS could be applied for detection of PGE in both, liquid and solid samples. However, so far only application to liquid samples, i.e., waters, digests, eluates and extracts of solids, were reported. This is obviously due to the numerous interferences that would have to be eliminated when applying direct solid sampling of complex, environmental matrices, like soils or dusts. Even tough sensitivity is significantly higher than in ICP-AES or FAAS, typically separation and pre-concentration from the liquid samples are performed prior to analysis by ETAAS. In comparison to ICP-MS detections limit are clearly higher, however, separation can be less selective, because possible spectral interferences are rare (Welz and Sperling 1997). A suitable combination of automated pre-concentration with ETAAS detection for determination of Pd in various environmental and biological samples after total digestion has been described by Schuster and Schwarzer (1996) and Leopold et al. (2008). The FIAS on basis of selective on-column pre-concentration has been described above and provides a detection limit of only 0.016 µg L^{-1} in combination with ETAAS. Sample amounts of approximately 100 mg are typically required. Due to the automated separation, pre-concentration and measurement this procedure is suitable for large sets of samples and has been applied to road dusts, sewage sludge ashes, soil samples, and plant samples (Battke et al. 2008; Leopold et al. 2008). The method has been successfully validated by investigation of certified reference material *Road Dust BCR-723*.

Another possible sample preparation prior to ETAAS detection for PGE determination in solid environmental samples is the nickel sulfide fire assay (Zereini et al. 2007). Here the gained NiS button is dissolved, as mentioned above, and the solution is measured subsequently by ETAAS. With this procedure it is possible to determine Pt, Pd and Rh. Os is not quantifiable due to volatilization during formation of the NiS button because of the high temperatures applied. (Urban et al. 1995). The method was validated by independently performed interlaboratory tests achieving detection limits of 0.5 µg Pd L^{-1}, 1.0 µg Pt L^{-1} and 0.7 µg Rh L^{-1} (Zereini et al. 2007). A limitation of this method is the high sample consumption (approx. 50 g) and the manual sample preparation steps.

4.5 Voltammetry

Square wave adsorption stripping voltammetry (SWAdSV) can generally be used to measure Pd, Pt, and Rh in aqueous samples. For Pd determination typically dimethylglyoxime is added as a ligand, whereas formaldehyde and hydrazine (formazone complex) are added for determination of Pt and Rh. In this regard, efficient mineralization of the sample is the most crucial preparation step since any organic matter strongly interferes the detection of the specific PGE-complexes (Zimmermann et al. 2003). Therefore, stripping voltammetry is mainly applied to water samples providing detection limits in the sub μg L^{-1} range. Locatelli (2006b) has reported an example for PGE detection in seawaters and fresh waters by SWAdSV achieving limits of detection of 0.019 μg Pd L^{-1}, 0.021 μg Pt L^{-1}, and 0.027 μg Rh L^{-1}. The method was verified by analysis of standard reference materials (*CCRMP–CANMET–TDB-1* and *CCRMP–CANMET–UMT-1* (rock soils), sea water *BCR-CRM 403* and fresh water *NIST-SRM 1643d*), however, in case of the water samples the reference materials were not certified for PGE concentrations but spiked with known concentrations. Orecchio et al. optimized an analytical method for biological matrices, using the differential pulsed voltammetry (DPV) to measure the concentration of Pt in blood and perfusate (Orecchio et al. 2012).

4.6 Chemiluminescence

Malejko et al. proposed an unusual approach for detection of Pt by means of chemiluminescence measurement (Malejko et al. 2010). Here, Pt(IV) ions are separated and pre-concentrated from a liquid sample on a bio-sorbent column in a flow injection system. The bio-sorbent column contains a Cellex-T resin (cellulose powder containing quaternary amine exchange groups) where green algae *C. vulgaris* cells are immobilized. During elution with lucigenin in alkaline solution chemiluminescence is measured. An increasing amount of Pt(IV) quenches the chemiluminescence of the green algae generated by lucigenin. Beside the advantage of a simple instrumental set-up, a detection limit of 0.1 μg Pt L^{-1} was achieved and the method could be successfully validated by investigation of the certified reference material *Road Dust BCR-723* (Malejko et al. 2010, 2012).

4.7 Neutron Activation Analysis

The NAA is a unique, very precise technique, but the requirement of a neutron source makes it unserviceable for routine measurement. Generally, the method is applicable to any environmental sample, liquid and solid. However, interferences

Table 2 Summary of analysis methods for separation, pre-concentration, and detection of platinum group elements in environmental samples (Including only work that has been published in 2005 and thereafter; [a]Sample matrix was spiked with analyte; [b]Detection of soluble fraction only; Abbreviations: ICP-MS, inductively coupled plasma mass- spectrometry; ETAAS, electro thermal atomic absorption spectrometry; FAAS, flame atomic absorption spectrometry; ID-ICP-MS, isotope dilution- inductively coupled plasma- mass spectrometry; LA-ICP-MS, laser ablation- inductively coupled plasma- mass spectrometry; NAA, neutron activation analysis)

Matrix		Pre-treatment	Separation and Pre-concentration	Detection technique	Detected or spiked[a] PGE concentrations [μg kg^{-1}] (unless stated otherwise)	Limit of detection [μg kg^{-1}] (unless stated otherwise)	References
Soils and Sediments	Urban soils	–	Nickel sulfide fire assay	ICP-MS	Pd: 0.45 49.79	Pd: 0.45	Mihaljevič et al. (2013)
					Pt: 0.72–159.50	Pt: 0.7	
					Rh: 0.08–3.86	Rh: 0.08	
					Ir: 0.09–0.28	Ir: 0.08	
	Roadside soils	Microwave-assisted digestion with HNO_3/HCl/HF	Flow-injection using RP-18 micro-column and selective ligand	ETAAS	Pd: 8–193	Pd: 5	Schindl et al. (2014)
		–	Nickel sulfide fire assay	ICP-MS	Pd: 1.31–120	NA	Pan et al. (2009)
					Pt: 2.59–160		
					Rh: 0.24–34.5		
		Microwave-assisted digestion with HNO_3, HF	Drying and re-dissolving	ETAAS	Pd: 3.8–7.3	Pd: 0.45	Tsogas et al. (2008)
					Pt: 46.3–113.2	Pt: 1.90	
					Rh: 10.8–15.8	Rh: 0.60	
		–	Nickel sulfide fire assay	ICP-MS	Pd: 0.41–43.3	Pd: 0.03	Wichmann et al. (2007)
					Pt: 0.10–50.4	Pt: 0.015	
					Rh: 0.08–10.7	Rh: 0.02	
		–	Nickel sulfide fire assay	ETAAS	Pd: 20–191	Pd: 0.5	Zereini et al. (2007)
					Pt: 41–254	Pt: 1.0	
					Rh: 7–36	Rh: 0.7	
		Microwave-assisted digestion with HNO_3/HCl; Filtration	Ion exchange resin	ICP-MS	Pd^b: 5.4–61.2	NA	Whiteley and Murray (2005)
					Pt^b: 9.0–103.8		
					Rh^b: 1.6–17.2		
	Spiked soil	Microwave-assisted digestion with HNO_3/HCl	Extracted with pyridine-functionalized	FAAS	Pd^a: 5 μg L^{-1}	Pd: 0.15 μg L^{-1}	Bagheri et al. (2012)

(continued)

Table 2 (continued)

Matrix		Pre-treatment	Separation and Pre-concentration	Detection technique	Detected or spiked[a] PGE concentrations [$\mu g\ kg^{-1}$] (unless stated otherwise)	Limit of detection [$\mu g\ kg^{-1}$] (unless stated otherwise)	References
			magnetic nanoparticles				
	Spiked soil extracts	Microwave-assisted digestion with HCl/ H_2O_2	Flow-injection using alumina-filled micro-column	ICP-AES	$Pd^{a,\ b}$, $Pt^{a,\ b}$, $Rh^{a,\ b}$: 2–5,000 $\mu g\ L^{-1}$	Pd: 0.7 $\mu g\ L^{-1}$	Herincs et al. (2013)
						Pt: 2.1 $\mu g\ L^{-1}$	
						Rh: 0.3 $\mu g\ L^{-1}$	
	Sediments	Mineralisation with HNO_3/HCl; Filtration	–	Adsorption stripping voltammetry	Pd^b: 5.9	Pd: 2.3	Locatelli (2006b)
					Pt^b: 28.6	Pt: 1.5	
					Rh^b: < LOD	Rh: 2.9	
	Road-deposited sediments	Digestion with aqua regia; Centrifugation	Cation exchange resin, Drying and re-dissolving	ICP-MS	Ir^b: 0.04–0.59	Ir: 0.01	Sutherland et al. (2007)
					Pd^b: 2.08–105	Pd: 0.03	
					Pt^b: 4.44–506	Pt: 0.03	
					Rh^b: 0.36–64.1	Rh: 0.01	
Dusts	Road dust	Digestion with aqua regia /H_2O_2, Filtration	On-column using modified multi walled carbon nanotubes as adsorption material	FAAS	Pd^b: 60–160	Pd: 0.3 $\mu g\ L^{-1}$	Afzali et al. (2012)
		Digestion with aqua regia; Centrifugation	Cation exchange resin	ICP-MS	Pd^b: 4.7–458.8	Pd: 0.2	Gao et al. (2012)
					Pt^b: 0.4–182.9	Pt: 0.5	
					Rh^b: 0.1–68.0	Rh: 0.09	
		Microwave-assisted digestion with HNO_3/ HCl/HF	Cation exchange resin; NH_3 collision gas	ICP-MS	Pd: 10–88	NA	Spada et al. (2012)
					Pt: 35–131		
					Rh: 6–8		
		Microwave-assisted digestion with aqua regia	Separation with RP-18 column Flow-injection using a Cellex-T resin micro-	Chemi-luminescence	Pt^b: 351.80	Pt: 0.1 $\mu g\ L^{-1}$	Malejko et al. (2010)

(continued)

Table 2 (continued)

Matrix		Pre-treatment	Separation and Pre-concentration	Detection technique	Detected or spiked[a] PGE concentrations [μg kg^{-1}] (unless stated otherwise)	Limit of detection [μg kg^{-1}] (unless stated otherwise)	References
			column with immobilized green algae				
		Microwave-assisted digestion with HNO_3, HF	Drying and redissolving	ETAAS	Pd: 6.6–13.7	Pd: 0.45	Tsogas et al. (2008)
					Pt: 69.3–131.6	Pt: 1.90	
					Rh: 12.7–42.8	Rh: 0.60	
		Aqua regia leaching	Ion exchange resin	ICP-MS	Pd^b: 31.3–189.3	NA	Leśniewska et al. (2006)
					Pt^b: 90.4–265.6		
		Microwave-assisted UV-digestion with HCl, H_2O_2, HF	Flow-injection using RP-18 micro-column and DEBT as selective ligand	ETAAS	Pd: 4.5–133	0.015 μg L^{-1}	Limbeck (2006)
	Road tunnel dust	Microwave-assisted digestion with HNO_3/HCl/HF, HNO_3 followed by open vessel procedure with $HCLO_4$, *aqua regia*	Cation exchange resin; NH_3 collision gas	ICP-MS	Pd: 770 ± 208	NA	Spada et al. (2012)
					Pt: 529 ± 13		
					Rh: 152 ± 52		
		Microwave-assisted digestion with HNO_3/HCl/HF	Flow-injection using RP-18 micro-column and DEBT as selective ligand	ETAAS	Pd: 14–516	Pd: 0.016 μg L^{-1}	(Leopold et al. 2008)
	Extracts of road dust with rainwater	Microwave-assisted UV-digestion with HCl, H_2O_2	Flow-injection using RP-18 micro-column and DEBT as selective ligand	ETAAS	Pd^b: 0.47–2.03	0.015 μg L^{-1}	Limbeck (2006)

(continued)

Table 2 (continued)

Matrix		Pre-treatment	Separation and Pre-concentration	Detection technique	Detected or spiked[a] PGE concentrations [μg kg^{-1}] (unless stated otherwise)	Limit of detection [μg kg^{-1}] (unless stated otherwise)	References
Rock Sewage sludge	Rock	Digestion with aqua regia in a Carius tube	Te co-precipitation; cation exchange resin	ID-ICP-MS	Pd: 0.07–0.82	Pd: 0.015	Ma et al. (2013)
					Pt: 0.14–0.89	Pt: 0.009	
					Rh: 0.01–0.06	Rh: 0.001	
					Ru: 0.01–0.22	Ru: 0.001	
					Ir: 0.01–0.11	Ir: 0.001	
	Rock	–	–	LA-ICP-MS	Pd: 0.02–5.42 mg kg^{-1}	NA	Osbahr et al. (2013)
					Pt: 0.07–10.34 mg kg^{-1}		
					Rh: 0.01–0.85 mg kg^{-1}		
	Synthesized rock reference materials	–	–	LA-ICP-MS	Pd: 1.5–248 mg kg^{-1}	NA	Gilbert et al. (2013)
					Pt: 17.4–184 mg kg^{-1}		
					Rh: 2.2–210 mg kg^{-1}		
					Ru: 13.6–204 mg kg^{-1}		
					Os: 0.7–72.7 mg kg^{-1}		
					Ir: 2.3–121 mg kg^{-1}		
	Rock reference materials	Digestion with HNO_3/HCl	Cation exchange resin; Drying and re-dissolving	ID-ICP-MS	Pd: 0.161–22.4	NA	Shinotsuka and Suzuki (2007)
					Pt: 0.169–7.39		
					Re: 0.023–0.801		
					Ru: 0.022–5.98		
					Os: 0.012–3.43		
					Ir: 0.016–2.83		
	Sewage	Microwave-assisted digestion with HNO_3/HCl/HF	Flow-injection using RP-18 micro-column and DEBT as selective ligand	ETAAS	Pd: 69–405	Pd: 0.016 μg L^{-1}	Leopold et al. (2008)
	sludge ash						
	Manta birostris (different organs)	Wrapped in a polyethylene film and packed into a “rabbit” irradiation capsule	–	NAA	Pd: 33–665	Pd, Pt, Rh: 1	Essumang (2010)
					Pt: 148–847		
					Rh: 7–145		

(continued)

Table 2 (continued)

Matrix		Pre-treatment	Separation and Pre-concentration	Detection technique	Detected or spiked[a] PGE concentrations [µg kg^{-1}] (unless stated otherwise)	Limit of detection [µg kg^{-1}] (unless stated otherwise)	References
Biota	Marine biota	Dried sample wrapped in a polyethylene film and packed into a “rabbit” irradiation capsule	–	NAA	Pd: 12–161	NA	Essumang et al. (2010)
					Pt: 5–128		
					Rh: 0.3–4		
					[pg m^{-3}] (unless stated otherwise)	[pg m^{-3}] (unless stated otherwise)	References
Airborne particular matter	Urban airborne particular matter	Microwave-assisted digestion with HNO_3/HCl/HF	Cation exchange resin	ICP-MS	Pd: 5.0–29.1	Pd: 0.93	Puls et al. (2012)
					Pt: 7.5–26.8	Pt: 0.50	
	Urban and rural airborne particular matter	Digestion in a high pressure asher with HNO_3/HCl Treated with HF	Pt: Te co-precipitation and He collision gas Rh: Te co-precipitation Pd: Hg co-precipitation and He collision gas	ID-ICP-MS (Pt, Pd) ICP-MS (Rh)	Pd: 0.1–683	Pd: 0.05	Zereini et al. (2012)
					Pt: 0.1–80.9	Pt: 0.88	
					Rh: 0.1–31.6	Rh: 0.3	
	Urban and rural airborne particular matter	Digestion in a high pressure asher with HNO_3/HCl Treated with HF	Hg co-precipitation, He collision gas	ID-ICP-MS	Pd: 0.06–102.8	Pd: 0.05	Alsenz et al. (2009)
	Urban airborne particular matter	–	Nickel sulfide fire assay	ICP-MS	Pt: 10.9–21.8	NA	Pan et al. (2009)
					Rh: 4.68–7.44		
	Urban airborne particular matter	–	Nickel sulfide fire assay	ICP-MS	Pd: 33.9–37.8	Pd: 0.03 µg kg^{-1}	Wichmann et al. (2007)
					Pt: 6–159	Pt: 0.015 µg kg^{-1}	
					Rh: 1.2–10	Rh: 0.02 µg kg^{-1}	
					[µg L^{-1}] (unless stated otherwise)	[µg L^{-1}] (unless stated otherwise)	

(continued)

Table 2 (continued)

Matrix		Pre-treatment	Separation and Pre-concentration	Detection technique	Detected or spiked^a PGE concentrations [μg kg^{-1}] (unless stated otherwise)	Limit of detection [μg kg^{-1}] (unless stated otherwise)	References
Waters	Surface water	Mineralisation with HNO_3/HCl; Filtration	–	Adsorption stripping voltammetry	Pd^b: 0.195	Pd: 0.019	Locatelli (2006b)
					Pt^b: 0.150–0.177	Pt: 0.021	
					Rh^b: < LOD	Rh: 0.027	
	Waste water	Filtration	On-column using modified multi walled carbon nanotubes as adsorption material	FAAS	Pd: 1.82–3.16	Pd: 0.3	Afzali et al. (2012)
	Spiked surface water	–	Anionic exchange resin	ETAAS	Pd: 0.13	NA	Li et al. (2012)
	Spiked surface water	Filtration	Extraction with pyridine-functionalized magnetic nanoparticles	FAAS	Pd$^{a,\ b}$: 5	Pd: 0.15	(Bagheri et al. 2012)
	Spiked river water	Microwave-assisted digestion with aqua regia	Flow-injection using a Cellex-T resin micro-column with immobilized green algae	Chemiluminescence	Pt^a: 1–5	Pt: 0.1	Malejko et al. (2010)

from long living ^{82}Br have to be considered in the case of Pd determination in bromine-rich environmental samples that can be avoided by separation techniques like nickel sulfide fire assay (Schwarzer et al. 2000). In contrast, biological samples that are usually low in bromine content can be measured directly without interferences. Here, NAA provides good detection limits in the low µg kg^{-1} range, for Pd, Pt, and Rh (Essumang 2010). Validation of this method was done by investigation of precious metal ore standard reference materials and gave overall uncertainty of 5 % (Essumang 2010).

5 Conclusions and Outlook

Reliable determination of PGE trace analysis in environmental and biological samples remains a challenging task. However, several analytical procedures combining various separation, pre-concentration, and detection techniques have been developed and tested within the last decade, but only few of them proved feasible approaches for investigation of real-world samples. Even though enhancements in sensitive instrumental techniques, like ICP-MS or ETAAS that generally allow higher selectivity and sensitivity for trace metals, this is not always the case for PGE analysis in complex matrices. Therefore, a main issue is still efficient separation and pre-concentration of PGEs prior to analysis. In this regard, automated and simultaneous or at least sequential systems are preferable over manual techniques, in order to make the procedures more suitable for larger sample series, which is a main requirement in environmental monitoring and toxicological studies.

Beside the development of novel analytical strategies, a key issue regarding PGE trace analysis is validation. Most reference materials (CRM) with certified PGE contents are geological samples, like rock samples or precious metal ores, with rather high PGE contents. The only certified reference material with trace contents of Pd, Pt and Rh in an environmental sample, a road dust, is *BCR-723 from IRMM*. In 2007 Sutherland gave an overview of analytical methods that were successfully validated by investigation of *BCR-723*. Other matrices like soils or biological materials with certified PGE traces are not available. Due to this lack of appropriate CRMs, verification of analytical data is frequently performed only by internal reference measurements like recovery experiments in spiked samples. As a result, the quality of validation experiments reported for new approaches is often below the usual standards in trace metal analysis. For establishing a new analytical procedure, application of another analytical method as a reference, and/or reference measurements by other laboratories are required when appropriate certified reference materials are not available.

References

Afzali D, Jamshidi R, Ghaseminezhad S, Afzali Z (2012) Preconcentration procedure trace amounts of palladium using modified multiwalled carbon nanotubes sorbent prior to flame atomic absorption spectrometry. Arab J Chem 5:461–466

Alsenz H, Zereini F, Wiseman CLS, Püttmann W (2009) Analysis of palladium concentrations in airborne particulate matter with reductive co-precipitation, He collision gas, and ID-ICP-Q-MS. Anal Bioanal Chem 395:1919–1927

Bagheri A, Behbahani M, Amini MM et al (2012) Preconcentration and separation of ultra-trace palladium ion using pyridine-functionalized magnetic nanoparticles. Microchim Acta 178:261–268

Battke F, Leopold K, Maier M et al (2008) Palladium exposure of barley: uptake and effects. Plant Biol 10:272–276

Boch K, Schuster M, Risse G, Schwarzer M (2002) Microwave-assisted digestion procedure for the determination of palladium in road dust. Anal Chim Acta 459:257–265

Borisov OV, Coleman DM, Oudsema KA, Carter RO III (1997) Determination of Platinum, Palladium, Rhodium and Titanium in automotive catalytic converters using inductively coupled plasma mass spectrometry with liquid nebulization. J Anal At Spectrom 12:239–246

Ely JC, Neal CR, O'Neill JA Jr, Jain JC (1999) Quantifying the platinum group elements (PGEs) and gold in geological samples using cation exchange pretreatment and ultrasonic nebulization inductively coupled plasma-mass spectrometry (USN-ICP-MS). Chem Geol 157:219–234

Essumang DK (2010) First determination of the levels of Platinum group metals in manta birostris (Manta Ray) caught along the ghanaian coastline. Bull Environ Contam Toxicol 84:720–725

Essumang DK, Adokoh CK, Boamponsem L (2010) Levels of Platinum group metals in selected species (Sarotherodon melanotheron, Chonophorus lateristriga, Macrobrachium vollenhovenii and Crassostrea tulipa) in some estuaries and lagoons along the coast of Ghana. Sci World J 10:1971–1987

Gao B, Yu Y, Zhou H, Lu J (2012) Accumulation and distribution characteristics of platinum group elements in roadside dusts in Beijing, China. Environ Toxicol Chem 31:1231–1238

Ghaseminezhad S, Afzali D, Taher MA (2009) Flame atomic absorption spectrometry for the determination of trace amount of rhodium after separation and preconcentration onto modified multiwalled carbon nanotubes as a new solid sorbent. Talanta 80:168–172

Gilbert S, Danyushevsky L, Robinson P et al (2013) A comparative study of five reference materials and the lombard meteorite for the determination of the platinum-group elements and gold by LA-ICP-MS. Geostand Geoanalytical Res 37:51–64

Gómez MB, Gómez MM, Palacios MA (2000) Control of interferences in the determination of Pt, Pd and Rh in airborne particulate matter by inductively coupled plasma mass spectrometry. Anal Chim Acta 404:285–294

Gómez MB, Gómez MM, Palacios MA (2003) ICP-MS determination of Pt, Pd and Rh in airborne and road dust after tellurium coprecipitation. J Anal At Spectrom 18:80–83

Herincs E, Puschenreiter M, Wenzel W, Limbeck A (2013) A novel flow-injection method for simultaneous measurement of platinum (Pt), palladium (Pd) and rhodium (Rh) in aqueous soil extracts of contaminated soil by ICP-OES. J Anal At Spectrom 28:354–363

Köllensperger G, Hann S, Stingeder G (2000) Determination of Rh, Pd and Pt in environmental silica containing matrices: capabilities and limitations of ICP-SFMS. J Anal At Spectrom 15:1553–1557

Leopold K, Maier M, Weber S, Schuster M (2008) Long-term study of palladium in road tunnel dust and sewage sludge ash. Environ Pollut Barking Essex 1987 156:341–347

Leśniewska BA, Godlewska-Żyłkiewicz B, Ruszczyńska A et al (2006) Elimination of interferences in determination of platinum and palladium in environmental samples by inductively coupled plasma mass spectrometry. Anal Chim Acta 564:236–242

Li L, Leopold K, Schuster M (2012) Effective and selective extraction of noble metal nanoparticles from environmental water through a noncovalent reversible reaction on an ionic exchange resin. Chem Commun 48:9165

Limbeck A (2006) Microwave-assisted UV-digestion procedure for the accurate determination of Pd in natural waters. Anal Chim Acta 575:114–119

Locatelli C (2006a) Simultaneous square wave stripping voltammetric determination of platinum group metals (PGMs) and lead at trace and ultratrace concentration level: Application to surface water. Anal Chim Acta 557:70–77

Locatelli C (2006b) Possible interference in the sequential voltammetric determination at trace and ultratrace concentration level of platinum group metals (PGMs) and lead: Application to environmental matrices. Electrochim Acta 52:614–622

Ma GS-K, Malpas J, Gao J-F et al (2013) Platinum-group element geochemistry of intraplate basalts from the Aleppo Plateau, NW Syria. Geol Mag 150:497–508

Malejko J, Godlewska-Żyłkiewicz B, Kojło A (2010) A novel flow-injection method for the determination of Pt(IV) in environmental samples based on chemiluminescence reaction of lucigenin and biosorption. Talanta 81:1719–1724

Malejko J, Szygałowicz M, Godlewska-Żyłkiewicz B, Kojło A (2012) Sorption of platinum on immobilized microorganisms for its on-line preconcentration and chemiluminescent determination in water samples. Microchim Acta 176:429–435

Matthey J (2012) Platinum 2012. Platin Met Rev 56:200–201

Messerschmidt J, von Bohlen A, Alt F, Klockenkämper R (2000) Separation and enrichment of palladium and gold in biological and environmental samples, adapted to the determination by total reflection X-ray fluorescence. Analyst 125:397–399

Mihaljevič M, Galušková I, Strnad L, Majer V (2013) Distribution of platinum group elements in urban soils, comparison of historically different large cities Prague and Ostrava, Czech Republic. J Geochem Explor 124:212–217

Orecchio S, Amorello D (2011) Platinum levels in urban soils from Palermo (Italy); Analytical method using voltammetry. Microchem J 99:283–288

Orecchio S, Amorello D, Carollo C (2012) Voltammetric determination of platinum in perfusate and blood: Preliminary data on pharmacokinetic study of arterial infusion with oxaliplatin. Microchem J 100:72–76

Osbahr I, Klemd R, Oberthür T et al (2013) Platinum-group element distribution in base-metal sulfides of the Merensky Reef from the eastern and western Bushveld Complex, South Africa. Miner Deposita 48:211–232

Pan S, Zhang G, Sun Y, Chakraborty P (2009) Accumulating characteristics of platinum group elements (PGE) in urban environments, China. Sci Total Environ 407:4248–4252

Puls C, Limbeck A, Hann S (2012) Bioaccessibility of palladium and platinum in urban aerosol particulates. Atmos Environ 55:213–219

Schindl R, Malle L, Maier M, Leopold K (2014) Mobility of traffic-related palladium emissions in soil and porous media. submitted

Schuster M, Schwarzer M (1996) Selective determination of palladium by on-line column preconcentration and graphite furnace atomic absorption spectrometry. Anal Chim Acta 328:1–11

Schwarzer M, Schuster M, von Hentig R (2000) Determination of palladium in gasoline by neutron activation analysis and automated column extraction. Fresenius J Anal Chem 368:240–243

Shinotsuka K, Suzuki K (2007) Simultaneous determination of platinum group elements and rhenium in rock samples using isotope dilution inductively coupled plasma mass spectrometry after cation exchange separation followed by solvent extraction. Anal Chim Acta 603:129–139

Simpson LA, Thomsen M, Alloway BJ, Parker A (2001) A dynamic reaction cell (DRC) solution to oxide-based interferences in inductively coupled plasma mass spectrometry (ICP-MS) analysis of the noble metals. J Anal At Spectrom 16:1375–1380

Spada N, Bozlaker A, Chellam S (2012) Multi-elemental characterization of tunnel and road dusts in Houston, Texas using dynamic reaction cell-quadrupole-inductively coupled plasma-mass spectrometry: evidence for the release of platinum group and anthropogenic metals from motor vehicles. Anal Chim Acta 735:1–8

Sutherland RA (2007) Platinum-group element concentrations in BCR-723: A quantitative review of published analyses. Anal Chim Acta 582:201–207

Sutherland RA, Pearson DG, Ottley CJ (2007) Platinum-group elements (Ir, Pd, Pt and Rh) in road-deposited sediments in two urban watersheds. Hawaii. Appl Geochem 22:1485–1501

Totland MM, Jarvis I, Jarvis KE (1995) Microwave digestion and alkali fusion procedures for the determination of the platinum-group elements and gold in geological materials by ICP-MS. Chem Geol 124:21–36

Tsogas GZ, Giokas DL, Vlessidis AG, Evmiridis NP (2008) On the re-assessment of the optimum conditions for the determination of platinum, palladium and rhodium in environmental samples by electrothermal atomic absorption spectrometry and microwave digestion. Talanta 76:635–641

Urban H, Zereini F, Skerstupp B, Tarkian M (1995) The determination of platinum-group elements (PGE) by nickel sulfide fire-assay: Coexisting PGE-phases in the nickel sulfide button. Fresenius J Anal Chem 352:537–543

Wedepohl K-H (1995) The composition of the continental crust. Geochim Cosmochim Acta 59:1217–1232

Welz B, Sperling M (1997) Atomabsorptionsspektrometrie, 4th edn. Wiley-VCH, Weinheim

Whiteley JD, Murray F (2005) Autocatalyst-derived platinum, palladium and rhodium (PGE) in infiltration basin and wetland sediments receiving urban runoff. Sci Total Environ 341:199–209

Wichmann H, Anquandah GAK, Schmidt C et al (2007) Increase of platinum group element concentrations in soils and airborne dust in an urban area in Germany. Sci Total Environ 388:121–127

Winge RK, Fassel VA, Peterson VJ, Floyd MA (1993) Inductively coupled plasma atomic emission Spectroscopy. An atlas of spectral information. Elsevier, Amsterdam

Zereini F, Alsenz H, Wiseman CLS et al (2012) Platinum group elements (Pt, Pd, Rh) in airborne particulate matter in rural vs. urban areas of Germany: Concentrations and spatial patterns of distribution. Sci Total Environ 416:261–268

Zereini F, Urban H, Lüschow H-M (1994) Zur Bestimmung von Platingruppenelementen (PGE) in geologischen Proben nach der Nickelsulfid-Dokimasie. Erzmetall 47:45–52

Zereini F, Wiseman C, Püttmann W (2007) Changes in Palladium, Platinum, and Rhodium Concentrations, and Their Spatial Distribution in Soils Along a Major Highway in Germany from 1994 to 2004. Environ Sci Technol 41:451–456

Zimmermann S, Messerschmidt J, von Bohlen A, Sures B (2003) Determination of Pt, Pd and Rh in biological samples by electrothermal atomic absorption spectrometry as compared with adsorptive cathodic stripping voltammetry and total-reflection X-ray fluorescence analysis. Anal Chim Acta 498:93–104

Part III
Occurrence, Chemical Behavior and Fate of PGE in the Environment

Brazilian PGE Research Data Survey on Urban and Roadside Soils

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Abstract Since the 1990s, investigations on the increase of platinum (Pt), palladium (Pd), and rhodium (Rh) levels in urban environments of big cities all over the world due to catalytic converters emissions have increased enormously, mainly in developed countries. Nevertheless, relatively few studies were performed in developing countries, such as Brazil. The state of São Paulo is the most populous and richest Brazilian state, and the city of São Paulo is the largest city in South America, and the 7th largest metropolitan region of the world. In this article, a discussion about the results obtained for the platinum group elements (PGE) Pt, Pd and Rh concentrations in soils adjacent to a major road in São Paulo state and in soils adjacent to seven main high density traffic avenues in the metropolitan region of São Paulo City are presented. Pt, Pd and Rh were found in much higher concentrations than PGE geogenic background, showing a catalytic converter origin. The platinum group elements levels obtained in São Paulo urban soils were much higher than those obtained for the roadside soils. Pd levels about seven times higher than the results obtained for the roadside soils were observed. The highest concentrations obtained for Pt (208 ng g^{-1}) and Rh (45 ng g^{-1}) were of about 12 and 5 times higher than the results obtained for the roadside soils. The results indicate that the PGE concentrations in São Paulo soils are directly influenced by traffic conditions. The concentrations of traffic-related elements such as Pb, Zn and Cu were also determined in the studied soils. Factorial analysis and cluster analysis discriminated the traffic related metals from PGE in the urban soils. However, in the roadside soils PGE were well correlated with Pb, Cu and Zn. The results obtained at present for PGE levels in São Paulo soils demonstrate the importance of continuous monitoring, since the rapid increase of the vehicular fleet in Brazil should also increase PGE emissions.

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1 Introduction

There is little information on platinum group elements (PGE) contamination in countries with growing economies, such as China, India or Brazil, in spite of the expending automobile industry in these countries. The automobile industry in China and India have grown at an average of more than 15 % over the past few years, and last year alone 30 % of world passenger car sales were from China and India (Sen 2013). Brazil has ended 2012 with a total vehicular fleet of about 80 million vehicles. According to the National Traffic Department, between September/2003 and September/2013, there was an increase of 123 % in the Brazilian vehicular fleet. On the other hand, the population growth between 2000 and 2010 was of 11.8 %. The number of passenger cars jumped from about 24.5 millions in 2001 to 50.2 millions in 2012, showing a growth of 104.9 %, being 44.4 % in the 15 main metropolitan regions and 10.8 % in the metropolitan region of São Paulo (Rodrigues 2013).

São Paulo state, Brazil, is the most populous and richest Brazilian state, with an estimate population of 43.6 million inhabitants (IBGE 2013). The city of São Paulo is the largest city in South America, and the 7th largest metropolitan region of the world. This metropolitan region has a population of about 20 million people and a vehicular fleet of about 8.5 million circulating motor vehicles in the city. These vehicles are, according to the Environmental Protection Agency of the State of São Paulo (CETESB 2013), the governmental agency of air quality control, the main source of air pollution. An estimate of 4.46 thousand ton/year of particulate matter (PM) is released into the atmosphere, and 50 % of this PM is the result of automotive vehicle emissions.

In the last decade there has been a growing interest in determining PGE in different environmental compartments after the introduction of automobile catalytic converters (Rauch et al. 2000; Jarvis et al. 2001; Gómez et al. 2001; Morton et al. 2001; Ely et al. 2001; Whiteley and Murray 2003; Riga-Karandinos et al. 2006; Sutherland et al. 2007; Pan et al. 2009; Mathur et al. 2011; Jackson et al. 2007; Prichard and Fischer 2012). Most studies had demonstrated increased concentrations of PGE at roadside environments providing evidence that automobile catalysts are the predominant source of PGE (Whiteley and Murray 2003).

Thus, due to the increase in the number of vehicles in the last decade in Brazil, a similar increase in the number of catalytic converters and accompanying PGE pollution is to be expected. Automobile catalytic converters appeared in Brazil in 1996, and contain about 1.5 g of PGE. Brazilian vehicles use gasohol, a mixture of gas and alcohol in a proportion of 8:2, and the catalytic converters have mainly Pd and Rh. This differs from Europe, where the three-way catalysts based on Pt and Rh with a ratio of 5:1, and the high temperature threeway catalyst, with variable combinations of Pt, Pd and Rh, are used (Fritsche and Meisel 2004). Since 1993, Pd has been increasingly used to substitute the Pt/Rh catalysts in automobile catalytic converters (Zereini et al. 2007). Therefore, possible environmental and human health consequences can be expected. Pd is the most mobile of all platinum metals as a result of its chemical properties and can be taken up by plants in considerably greater amounts than Pt and Rh (Zereini et al. 2001). Ek et al. (2004) reported that evidence indicates that the PGE, especially Pd, are transported to biological materials, in this case, plants, through deposition in roots by binding to sulphur-rich low molecular weight species. PGE uptake to exposed animals showed that liver and kidney accumulate the highest levels of PGE, especially Pd. The PGE concentration in human urine and blood has been investigated in several studies. In road construction workers, the urinary Pt level was 0.9 ng l^{-1} and the Pd level was 52.2 ng L^{-1}. The urinary Pd level was below 10 ng L^{-1} in unexposed individuals. Urinary Pd and Rh, but not Pt, levels were correlated with traffic intensity. Adults from a large city (Rome) with dense traffic had greater urinary Pt and Rh concentrations than adults from a smaller town (Foligno) with relatively low traffic density, but no clear trend was found for Pd. In contrast, a significant correlation between urinary Pd and Rh concentrations and traffic density was found in children, but no correlation was observed for Pt (Yajun et al. 2012).

Risk assessments to human health of exposures to PGE, especially through inhalation of PGE-associated airborne particulate matter (PM), have been recently investigated. Colombo et al. (2008) studied the potential pathways of PGEs from vehicle exhaust catalysts into humans, by using a physiologically based extraction test (PBET) to verify the uptake of PGEs by the human digestive tract. These authors reported that solubilization of PGEs in the human digestive tract could involve the formation of PGE-chloride complexes, which are known to have toxic and allergenic effects.

Zereini et al. (2012) simulated human lung fluids; [artificial lysosomal fluid (ALF) and Gamble's solution] were used to assess the mobility of Pt, Pd and Rh in airborne PM of human health concern. Airborne PM samples (PM_{10}, $PM_{2.5}$, and PM_1) were collected in Frankfurt and Main, Germany. The mobility of PGE in airborne PM_1 samples was notable, with a mean of 51 Rh, 22 Pt, and 29 Pd present in PM_1 being mobilized by ALF after 24 h.

There has been little research on PGE levels in Brazil. da Silva et al. (2008) determined Pd and Rh, as well as other elements, such as Cd, Ce, Cu, La, Mo, Ni and Pb, in 24-h PM_{10} samples collected in five locations with different traffic densities and anthropogenic activities in Rio de Janeiro, Brazil. The results suggest that vehicular traffic is the most important source of environmental pollution at the studied sites.

There is little information about PGE levels in São Paulo soils, and almost none concerning Brazilian soils. With an expected continuous growth of the Brazilian vehicular fleet, and the implementation of the PGE based catalytic converters, there is a growing interest in studies of assessment of PGE in the environment. This chapter presents a survey of the studies performed in São Paulo roadside and urban soils (Morcelli et al. 2005; Ribeiro et al. 2012a), to assess PGE and the relationship between the results obtained and the catalytic converter abrasion. The elements Ba, Ce, Cu, La, Mo, Ni, Pb and Zn were also determined and their correlation with PGE is discussed.

2 Materials and Methods

Roadside soils from a major road (SP348), with high traffic flow (ca. 30,000 vehicles/day), running between São Paulo city and another important industrial regions of São Paulo State, and soils adjacent to the most important traffic arteries of São Paulo city were studied. For the roadside soils, the sampling strategy was based on a rectangular grid, in which composite samples were prepared by taking five samples that were collected at 1 m, along the 4-m stretch of the road. The sampling took place on a 40-cm grass strip beside the asphalt and up to 540 cm from the roadway. High-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) with NiS fire assay collection and Te coprecipitation was used as analytical procedure. Sampling was undertaken in October 2002 (Morcelli et al. 2005). For the street soils of São Paulo city, sampling was performed between October/2007 and February/2008. Seven important avenues were chosen based on varying traffic volumes and driving styles (stop and go and high constant speed). Areas of 1 m^2, forming a rectangular grid, were sampled. Composite samples were prepared, from three samples, collected at each point of the rectangle. Sampling took place from the grass strip 15 cm beside the asphalt up to 115 cm from the roadway. The sampling depth was 5 cm. Soils were digested with aqua regia in an ultrasonic bath at 65 °C for 35 min. Samples were centrifuged ($t = 10$ min and rpm = 3,000). The solutions obtained were transferred to Teflon beakers and the procedure was repeated with the solid residue. Samples were evaporated to dryness and diluted in HNO3 2 %. PGE levels were determined by ICP MS technique (Ribeiro et al. 2012a), while the other metals (Cu, Mo, Ni, Pb and Zn) concentrations were quantified by ICP OES technique (VARIAN, Model 710 ES). For the non-PGE elements, the quality control of the data was performed by analyzing the reference material SOIL 7 (IAEA). The results obtained for three replicates showed relative errors below 10 % and coefficients of variation better than 5 %. The elements Ba and Zn, and the lanthanides La and Ce were determined by instrumental neutron activation analysis (INAA). The analytical procedure is described in Ribeiro et al. (2012b).

3 Results

3.1 PGE Levels and Behavior

A summary of the results obtained for Pd, Pt and Rh in the studied soils, compared to other studies all over the world, is shown in Table 1. The obtained values showed a significant enrichment in relation to the continental crust levels ((Pd: 0.4 ng g-1; Rh: 0.06 ng g-1; Pt: 0.4 ng g-1, Wedepohl 1995). These values have been used as background values for PGE in several environmental studies (Zereini et al. 2005; Orecchio and Amorello 2011).

Table 1 Pt, Pd, and Rh levels in soils in different countries (literature data)

City/sampling year	Location	Pd (ng g^{-1})	Pt (ng g^{-1})	Rh (ng g^{-1})	References
Mexico City, Mexico	Roadside High density stop and go traffic High constant speed traffic densities	46.8–74 15.2–101.1	307.5–332.7 91.2–207.7	26–39.1 7.8–22.7	Morton et al. (2001)
Rome, Italy, 2001	Urban area		7.0–19.4		Cinti et al. (2002)
Napoli, Italy, 2000	Urban and suburban areas	8–110	1.6–52		Cicchella et al. (2003)
Perth, Australia, 2002–2003	Roadside	13.79–108.45	30.96–153.20	3.47–26.55	Whiteley and Murray (2003)
Athens, Greece, 2003	Highway roads Urban roads	25.4–236 20.3–185	73.3–254 34–216	–	Riga-Karandinos et al. (2006)
Braunschweig, Germany, 2005	Roadside High constant speed traffic densities High density stop and go traffic[a]	14.4–43.3 124	29.5–50.4 261	5.98–10.7 38.9	Wichmann et al. (2007)
Oxfordshire and London, England, 2000	Roadside	84.2–120.8	2.04–15.9	3.5–22.4	Hooda et al. (2007)
Hong Kong, China, 2007	Urban environments	6.93–107	15.4–160	1.61–34.5	Pan et al. (2009)
Palermo, Italy, 2010	Urban area		0.6–2240		Orecchio and Amorello (2011)
Seoul, Korea, 2008	Roadside		0.7–221		Lee et al. (2012)
São Paulo, Brazil, 2002	Roadside	1–58	0.3–17	0.1–8.2	Morcelli et al. (2005)
São Paulo, Brazil, 2007 and 2008	Highly dense traffic urban avenues	3–378	1–208	0.2–45	Ribeiro et al. (2012a)

[a] Highest concentration

As can be seen in Table 1, the highest results obtained for Pd and Rh concentrations in São Paulo urban soils were higher than those obtained in the other cities. Pt levels were at the same level as obtained for cities as Seoul, Mexico city and Athens.

On the other hand, the results obtained for the São Paulo urban soils were much higher than the results obtained for the São Paulo roadside soils. Pd levels about seven times higher than the results obtained for the roadside soils were observed. The highest concentrations obtained for Pt (208 ng g^{-1}) and Rh (45 ng g^{-1}) were of about 12 and 5 times higher than the results obtained for the roadside soils. These results can be explained by the traffic characteristics of the studied avenues. The highest levels were obtained in one avenue which presents stop & go traffic all day long, which can explain the high PGE concentrations obtained in the soil next to this avenue in relation to the other avenues, which alternates between constant speed and stop & go traffic flow.

Whiteley (2004) and Ward and Dudding (2004) reported the influence of traffic density and flow conditions in the PGE particle release and accumulation in the adjacent motorway environment. Wichman et al. (2007) observed a significant difference between the concentration levels of Pt, Pd and Rh in soils collected at one road outside the city of Braunschweig, Germany, where traffic moved with a constant speed, and a crowded street in the centre of Braunschweig with stop and go traffic (Table 1). Mathur et al. (2011) studied road dusts from Hyderabad city, India, along city roads with heavy, medium and low traffic and under different driving conditions. The highest PGE levels were observed at high traffic density, busy roads. The more pronounced PGE concentrations was attributed to the very high frequency of traffic jams, with many vehicles undergoing stop/start and variable speed conditions. Speed variation can damage the catalyst material due to large temperature gradients resulting in abrasion of the catalyst and release of PGE to the roadway environment. It is well established that maximum emission of PGE from the catalyst's surface occurs at frequent speed changes of the vehicle or with repeated stop and go conditions rather than from vehicles moving at constant average speed (Ward and Dudding 2004; Mathur et al. 2011). Lee et al. (2012) observed a remarkable difference in average Pt level between heavy traffic roads (av. 132.2 ng/g) and light traffic roads (av. 22.8 ng/g) in road dusts from Seoul.

The high PGE concentrations observed in the present study may be associated to the São Paulo traffic style and to the rapid increase of the vehicular fleet over the last years. Thus, as there has been a continuous growing in the number of circulating vehicles in São Paulo, an increase in PGE levels in São Paulo should be expected.

Zereini et al. (2007) in comparing PGE concentrations in soil samples collected along a major highway in Germany in 1994 and 2004, observed concentrations of Pd about 15 times higher on average than those measured in 1994. Pt and Rh concentrations increased 2 and 1.6 times, respectively, during this time period. Zereini et al. (2012), observed a significant increase in PGE concentrations in fractionated airborne dust (PM) collected in 2002 and in 2008–2010, in Frankfurt, Germany (increases of 12, 6 and 3 times for Pd, Pt and Rh, respectively). This reflects an increased use of Pd as an active catalyst in automobiles.

Wichmann et al. (2007) compared PGE analytical data, all generated in 1999 and in 2005 in the same sampling sites located mainly close to heavily used roads in the region of Braunschweig, an urban area in Germany. The comparison revealed a distinct increase of PGE concentrations in soils along heavy traffic roads by a factor of 2.1–8.9; once even a factor of 15 was determined.

Similarly to the results obtained in other studies (Schafer and Puchelt 1998; Morton et al. 2001), higher PGE concentrations were observed in the vicinity of roadways in São Paulo. The highest concentrations were found at 40 cm from the roadway. At about 140 cm of the roadway the concentrations are ca. 90 % lower compared to the samples collected at 40 cm from the road. This indicates the anthropogenic origin of the PGE.

For the adjacent soils of main avenues in São Paulo city, Pt, Pd and Rh presented higher concentrations in the samples collected at 15 cm from the asphalt, in 4 of the 7 studied avenues. Brown (2002) investigated the spatial distribution of the PGE in UK soils, comparing the levels of PGE in superficial soil samples (0–2 cm to 2–10 cm). Besides this, the author also considered the distance from the road. Samples were collected from the asphalt to a distance of 10 m. A decrease of about 12 times for Pt concentration and of about 9 times for Rh concentration with depth was observed. In the case of Pd, the concentration at 20 cm was about half of its level at the top samples. In relation to the distance, no change in concentration was observed up to a distance of 1.20 m. Nevertheless, from a distance of 2 m, there was a decrease of 60, 70 and 65 % in the concentration levels of Pd, Pt and Rh, respectively (Brown 2002). Wichmann et al. (2007) also reported the highest PGE concentrations in soils close to a road in Germany, declining exponentially with growing distance.

3.2 PGE Ratio

The PGE ratio (Pt/Pd; Pt/Rh; Pd/Rh) is an important indicator of the catalytic converter source (Jarvis et al. 2001; Whiteley 2005). The three-way catalysts based on Pt and Rh with a ratio of 5:1 and the high temperature three-way catalyst with variable combinations of Pt, Pd and Rh (e.g. 5:1 in a Pd/Rh catalyst or 1:14:1 in a Pt/Pd/Rh catalyst) have been widely used (Fritsche and Meisel 2004). Nevertheless, the development of new technologies for catalytic converter production and the replacement of Pt by Pd in the catalytic converter composition have changed the PGE concentrations in the environment. There has been a gradual shift of Pt based catalysts to Pd usage in the late 1990s and an introduction of only Pt, Pd–Rh, and Pd only or Pt–Pd–Rh catalysts. As a result, Pt/Pd and Pd/Rh ratios, derived from environmental samples analyzed, are non-uniform today (Wichmann et al. 2007).

In spite of the great increase of Pt and Pd concentrations in relation to the results obtained in roadside soils of São Paulo, the Pt/Pd ratios obtained in urban soils (0.2–0.4) did not differ much from the ratios obtained for the roadside soils, of 0.3–0.4. The results were lower than those obtained by Mathur et al. (2011), 0.3–7.5, lower than the values reported by Ely et al. (2001), 1.0–2.5, in soils along

U.S roads, and by Jarvis et al. (2001), that found a mean ratio of Pt/Pd of 6.6 and a range from 2.01 to 26.6 in road dust and surface samples adjacent to major UK roads. A lower concentration of Pt in Brazilian soils is expected, since the catalyst converters in Brazil contain mainly Pd and Rh.

The Pt/Rh ratio in the São Paulo roadside soils São Paulo was relatively constant, at 1.7 with a range from 0.54 to 4.7. The Pt/Rh ratios in São Paulo urban soils were more variable, with a range from 3.0 to 7.8, which agrees with the Pt/Rh ratios obtained in other autocatalyst-derived PGE studies. These values are in the range of 4.2–9.1 obtained in soils along a main highway in Germany (Zereini et al. 2007), of 5–16 given by Ely et al. (2001), but are lower than the Pt/Rh obtained by Fritsche and Meisel Meisel (2004), in soils along Austrian motorways (10.2–11.8) (Fritshe e Meisel 2004). Bocca et al. (2006) obtained Pt/Rh ratios ranging from 2.1 to 8.1 in urban aerosols from Buenos Aires, Argentina. The average Pt/Rh ratio of 5.1 ± 0.9 (range 4.0–9.0) is characteristic of autocatalyst emissions.

The relatively large variability of the Pt/Rh ratios compared with the Pt/Pd ratios suggests a significant difference in chemical behavior between Rh and Pd. Parry and Jarvis (2006) have observed that the ratios of Pt/Rh had decreased on UK roads from 1998 to 199, compared to values in 1995/1996, indicating a reduction of about 30 % in Pt compared to Rh and an increase in Pd of about 40 %. This may indicate that there is no apparent solubility difference between Rh and Pt in the environments studied, suggesting that not only are Pt and Rh associated during emission but they remain associated during any subsequent mobilization (Whiteley 2005).

The urban soil ratio Pd/Rh ranged from 10.6 to 25.4 which are much higher than the Pd/Rh ratios found by da Silva et al. (2008), in 24-h PM_{10} collected in five locations in the city of Rio de Janeiro, which ranged from 4.0 to 7.3, with an overall mean of 5.9. The 10.6–25.4 range is also higher than that for roadside soils from São Paulo (Morcelli et al. 2005) (0.4–5.4 m distance from roads), which ranged from 2 to 20, with a mean of 7.2. Zereini et al. (2007) obtained Pd/Rh ranging from 1.6 to to 8.4, Whiteley (2005) obtained ratios ranging from 1.7 to 8.7, and Ely et al. (2001), from 4 to 9, which may indicate the replacement of Pt by Pd in autocatalysts. Different types of catalytic converters are now available in the market, such as Pt only, Rh-Pd, Pd only or Pt-Pd-Rh catalysts. Since Pd appears to be the most mobile of all platinum metals, concerns are now being raised about possible environmental and human health consequences and risks.

3.3 *Other Metals Present in the Soil and Their Correlation with Pt, Pd and Rh*

Traffic derived trace elements (Ba, Ce, Cu, La, Mo, Ni, Pb, and Zn) were also analyzed in the studied roadside and urban soils (Table 2). These metals are usually associated with high traffic densities, originating from exhaust emissions, tires, braking, vehicle and engine wear, and/or the re-suspension of road dusts (Peachey et al. 2009).

Table 2 Metal range concentration in São Paulo roadside and urban soils

Element	Range (mg kg^{-1})	
	Urban soils of São Paulo City	Roadside soils (40 cm up to 140 cm from the roadway)
Ba	105–713	259–2221
Cu	3–838	27–110
Mo	1–6	<1–4.9
Ni	1–152	16–31
Pb	6–470	46–153
Zn	58–1669	170–592
La	14–90	29–61
Ce	3–186	58–233

For a better comparison of the behavior of the PGE and the other traffic-related elements in the roadside and the urban soils studied, a statistical approach was employed. Figure 1 shows the hierarchical dendrograms obtained by cluster analysis of the data set (PGE and other elements) obtained for the roadside soils (Fig. 1a) and for the urban soils (Fig. 1b). In this approach, the data obtained up to 140 cm for the roadside soils were used, since it was up to this distance that there was more influence of the vehicular emissions (Morcelli et al. 2005).

For the roadside soils (Fig. 1a), two main groups can be identified. The first group is integrated by two sub-groups that are strongly associated: PGE, Cu, Pb and Zn are included in one sub-group and Mo and Ni in another sub-group. The second group includes Ba, La and Ce. The correlation of the PGE and Pb, Cu and Zn can be explained by the fact that Pb, Cu and Zn are metals known to be associated with motor vehicle pollution. Copper is added as an antioxidant and may be present in the coarse fraction of the particles originating from the wearing down of engine bearings or other components. Zn is associated with the use of additives and lubricants (da Silva et al. 2010). The strong association between Mo and Ni may be

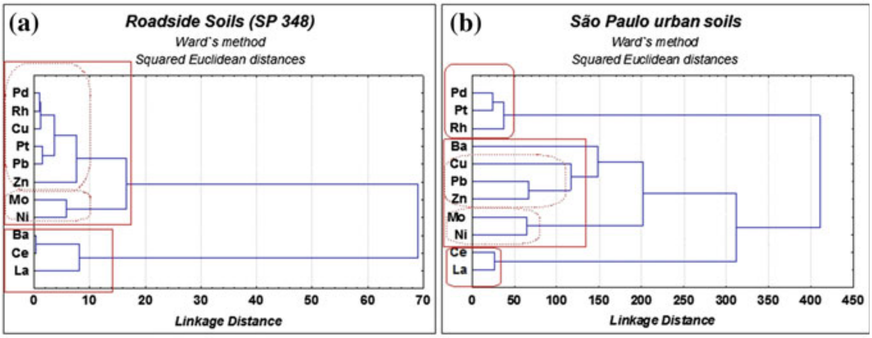

Fig. 1 Hierarchical dendrograms obtained by cluster analysis of the PGE and traffic-related element concentrations in the roadside soils (**a**) and in the urban soils (**b**) of São Paulo

due to the fact that these elements are used to coat cylinders of diesel vehicle motors (Tomanik 2000). Table 2 shows that lead levels were comparable to other studies (9–154 mg/kg, Tsogas et al. 2009) indicating the influence of car traffic on its accumulation in roadside soils. The other metals presented similar levels to other populous cities, such as Athens and Mexico City (Morton et al. 2001; Riga-Karandinos et al. 2006).

The correlation between PGE and Pb has already been reported in other studies. Riga-Karandinos et al. (2006) obtained a positive correlation between Pt and Pb (r = 0.436) but not very high, while no correlation between Pd and Pb was demonstrated.

Ba, La, and Ce are present as additives in catalytic converters. La and Zr oxides are added to the washcoat as stabilizers (Rauch et al. 2000). Ce, employed as a promoter in catalytic converters, is used in a Ce/Pt ratio of about 20–100 (Zereini et al. 2001). Nevertheless, no correlation was observed between PGE and Ba, La and Ce.

A constant La/Ce ratio was obtained for all samples in São Paulo roadside and urban soils indicating a soil origin (Morcelli et al. 2005). As observed by Jarvis et al. (2001), the background concentrations of Ce in soil are typically many tens of $\mu g\ g^{-1}$ and the addition of autocatalyst derived particulate containing Ce to this system can hardly change the background.

The hierarchical cluster obtained for the urban soils data set (PGE and other elements) (Fig. 1b) compared to the dendrogram obtained for the roadside soils (Fig. 1a), shows a slight difference in the distribution of the studied elements. In Fig. 1b, three main groups are identified. The first group is integrated only by the PGE: Pt, Pd and Rh. A second cluster group includes Cu, Pb, Zn, Mo and Ni, with Ba less correlated, while La and Ce are separated in the third group. One possible explanation for the fact that the PGE did not correlated with Pb, Cu and Zn as strongly as observed for the roadside soils (Fig. 1a), is that in street soils of São Paulo, the wear and tear of certain automobile materials and parts during driving are more intense, due to the higher density of traffic in São Paulo city and the stop and go conditions rather than vehicles moving at constant average speeds. This can favor the release of traffic-related elements such as Cu and Zn rather than PGE, which originate from automotive catalysers.

Factorial analysis (FA) with extraction principal components, using the Windows STATISTIC® 8.0 program, was applied to the results obtained for Pt, Pd and Rh and the other elements determined in São Paulo urban soils. Kaiser criterion (Yeomans and Golder 1982) was used to assess the results of initial eigenvalues (Table 3). Applying the varimax-raw rotation, three principal components were considered, which accounted for about 72 % of the total variance. The matrix of the components for data set indicated that Pt, Pd and Rh presented strong correlation and were associated into the first component (F1), with a factor loading of ≥0.96. This result indicates that these elements have the same source, catalytic converter exhausts. As observed in the cluster analysis (Fig. 1b), the elements Ba, Ce and La were grouped, presenting the highest factor loads associated to factor 2. The higher Cu, Mo, Ni, Pb and Zn factor loads were observed in Factor 3, indicating a common

Table 3 Factor loadings, eigenvalues and total variance (%)

Variables	Factor 1	Factor 2	Factor 3
Pd	0.93	−0.01	0.08
Pt	0.96	−0.07	0.05
Rh	0.90	0.03	0.14
Ba	0.05	0.66	0.31
Cu	0.24	0.03	0.61
Mo	0.08	0.03	0.84
Ni	0.04	−0.05	0.79
Pb	0.18	0.33	0.65
Zn	0.47	0.28	0.72
Ce	−0.06	0.93	0.05
La	0.03	0.94	0.03
Eigenvalues	4.07	2.38	1.48
(%) Total variance	36.99	21.59	13.49
(%) Cumulative	36.99	58.58	72.08

origin, apparently associated to general motor wear. These metals are present in the chemical composition of automotive fuels, such as diesel and gasoline, or as impurities in the alcohol used as vehicle fuel in Brazil. Thus, Factorial Analysis showed that, even though the analyzed elements are originated from automotive emissions, it was possible to distinguish the automotive catalyser source (Pd, Pt e Rh) and the fuel oils and other parts of the vehicles origin (Cu, Mo, Ni, Pb, and Zn).

The results indicate that, although the vehicular emissions must be the main source of Pd, Pt, Rh, Ba, Cu, Mo, Ni, Pb and Zn in urban soils adjacent to São Paulo city avenues, no significant correlation was obtained between the PGE elements and other traffic-related elements determined. These results differ from the results obtained for the São Paulo roadside soils and from other studies. Ely et al. (2001) studying the Pd, Pt and Rh behavior in urban environments verified a strong correlation with the metals Ni, Cu, Zn and Pb. Schäfer and Puchelt (1998) observed positive correlations between the PGE and Zn, Cu and Pb. On the other hand Zereini et al. (2001) and Whiteley (2004) have observed no correlations between PGE and Pb.

4 Conclusions

In soils next to roads and avenues in São Paulo, Pt, Pd and Rh were found in much higher concentrations than PGE geogenic background. These high concentrations indicate catalytic converter origin. The PGE levels obtained in São Paulo urban soils were much higher than those obtained for roadside soils adjacent to a major road in São Paulo. This may be attributed to the São Paulo traffic density and style and to the rapid increase of the numbers of cars equipped with catalytic converters circulating in the city in the last years. The results of this study further indicate that the PGE concentrations in São Paulo soils are directly influenced by traffic conditions and distance. Lower levels of Pt/Pd ratios compared to other similar studies were observed due to the different Pt/Pd/Rh ratio in Brazilian automobile catalytic converters.

In São Paulo roadside soils, Pb, Cu and Zn showed positive correlations with Pt, Pd and Rh. In contrast, in São Paulo urban soils, these correlations were not observed. This indicates that in the urban soils studied, it was possible to distinguish the automotive catalyser source (Pd, Pt e Rh) and the fuel oils and other parts of the vehicles origin (Cu, Pb and Zn).

The results obtained at present for PGE levels in São Paulo soils demonstrate that, with the rapid increase of the vehicular fleet in Brazil, and the use of cars equipped with PGE based catalytic converters, PGE emissions are expected to soon increase.

The potential risk to human health due to the presence of PGE in the environment is not at present well established. Therefore, it is extremely important to continue monitoring PGE levels, their mechanisms of migration, accumulation and bio effects, mainly in developing countries such as Brazil.

References

Bocca B, Caimi S, Smichowski P, Gómez D, Caroli S (2006) Monitoring Pt and Rh in urban aerosols from Buenos Aires. Argentina Sci Total Environ 358:255–264

Brown RA (2002) Environmental impact of platinum, palladium and rhodium in the roadside environment. PhD [Thesis]. Imperial College, Londres, UK

CETESB (São Paulo) Qualidade do ar no estado de São Paulo 2012 / CETESB. São Paulo: CETESB, 2013. (Série Relatórios/Secretaria de Estado do Meio Ambiente, ISSN 0103–4103), 123 Available from. http://www.cetesb.sp.gov.br/ar/qualidade-do-ar/31-publicacoes-e-relatorios. Accessed 28th February 2014

Cicchella D, DeVivo B, Lima A (2003) Palladium and platinum concentration in soils from the Napoli metropolitan area, Italy: possible effects of catalytic exhausts. Sci Total Environ 308:121–131

Cinti D, Angelone M, Masi U, Cremisini C (2002) Platinum levels in natural and urban soils from Rome and Latium (Italy): significance for pollution by automobile catalytic converter. Sci Total Environ 293:47–57

Colombo C, Monhemius AJ, Plant JA (2008) The estimation of the bioavailabilities of platinum, palladium and rhodium in vehicle exhaust catalysts and road dusts using a physiologically based extraction test. Sci Total Environ 389:46–51

Da Silva MF, Assunção JV, Andrade MF, Pesquero CR (2010) Characterization of metal and trace element contents of particulate matter (PM_{10}) emitted by vehicles running on Brazilian fuels—hydrated ethanol and gasoline with 22 % of anhydrous ethanol. J Toxicol Env Health 73:901–909 da Silva LID, Sarkis JES, Zotin FMZ, Carneiro MC, Alcover-Neto A, Da Silva ASAG, Cardoso MJB, Monteiro MIC (2008) Traffic and catalytic converter—related atmospheric contamination in the metropolitan region of the city of Rio de Janeiro, Brazil. Chemosphere 71:677–684

Ek KH, Morrison GM, Rauch S (2004) Environmental routes for platinum group elements to biological materials—a review. Sci Total Environ 334–335:21–38

Ely JC, Neal CR, Kulpa CF, Schneegurt MA, Seidler JA, Jain JC (2001) Implications of platinum-group element acumulation along U.S. roads from catalytic-converter attrition. Environ. Sci. Techno. 35:3816–3822

Fritsche J, Meisel T (2004) Determination of anthropogenic input of Ru, Rh, Pd, Re, Os, Ir and Pt in soils along Austrian motorways by isotope dilution ICP-MS. Sci Total Environ 325:145–154

Gómez B, Gómez M, Sanchez JL, Fernández R, Palacios MA (2001) Platinum and rhodium distribution in airbone particulate matter and road dust. Sci Total Environ 269:131–144

Hooda PS, Miller A, Edwards AC (2007) The distribution of automobile catalyst-cast platinum, palladium and rhodium in soils adjacent to roads and their uptake by grass. Sci Total Environ 384:384–392

IBGE—Instituto Brasileiro de Geografia e Estatística. Censo 2010. Available from http://www.cidades.ibge.gov.br/xtras/perfil.php?codmun=355030%26search=sao-paulo|sao-paulo&lang. Accessed form 20th February 2014

Jackson MT, Sampson J, Prichard HM (2007) Platinum and palladium variations through the urban environment: Evidence from 11 sample types from Sheffield. UK. Sci. Total Environ 385:117–131

Jarvis KE, Parry SJ, Piper JM (2001) Temporal and spatial studies of autocatalyst-derived platinum, rhodium and palladium and selected vehicle-derived trace elements in the environment. Environ Sci Technol 35:1031–1036

Lee HY, Chon HT, Sager M, Marton L (2012) Platinum pollution in road dusts, roadside soils, and tree barks in Seoul, Korea. Environ Geochem Health 34:5–12

Mathur R, Balaram V, Satyanarayanan M, Sawant SS, Ramesh SL (2011) Anthropogenic platinum, palladium and rhodium concentrations in road dusts from Hyderabad city, India. Environ Earth Sci 62:1085–1098

Morcelli CPR, Figueiredo AMG, Sarkis JES, Kakazu M, Enzweiler J, Sigolo JB (2005) PGEs and other traffic related elements in roadside soils from São Paulo. Brazil. Sci. Total Environ. 345:81–91

Morton O, Puchelt H, Hernandez E, Lounejeva E (2001) Traffic-related platinum group elements (PGE) in soils from Mexico City. J Geochem Explor 72:223–227

Orecchio S, Amorello D (2011) Platinum levels in urban soils from Palermo (Italy); Analytical method using voltammetry. Microchem J 99:283–288

Pan S, Zhang G, Sun Y, Chakraborty P (2009) Accumulating characteristics of platinum group elements (PGE) in urban environments, China. Sci Total Environ 407:4248–4252

Parry SJ, Jarvis KE (2006). Temporal and spatial variation of palladium in the roadside environment. In: Zereini F, Alt F (eds) Palladium emissions in the environment: analytical methods, environmental assessment and health effects. Springer, New York, pp 419–432

Peachey CJ, Sinnett D, Wilkinson M, Morgan MGW, Freer-Smith PH, Hutchings TR (2009) Deposition and solubility of airborne metals to four plant species grown at varying distances from two heavily trafficked roads in London. Environ Pollut 157:2291–2299

Prichard HM, Fischer PC (2012) Identification of platinum and palladium particles emitted from vehicles and dispersed into the surface environment. Environ Sci Technol 46:3149–3154

Rauch S, Morrison GM, Motelica-Heino M, Donard OFX, Muris M (2000) Elemental association and fingerprint of traffic-related metals in road sediments. Environ Sci Technol 33:3119–3323

Ribeiro AP, Figueiredo AMG, Sarkis JES, Hortellani MA, Markert B (2012a) First study on anthropogenic Pt, Pd, and Rh levels in soils from major avenues of São Paulo City, Brazil. Environ Monit Assess 184:7373–7382

Ribeiro AP, Figueiredo AMG, Ticianelli RB, Nammoura-Neto GM, Silva NC, Kakazu MH, Zahn G (2012b) Metals and semi-metals in street soils of São Paulo city, Brazil. J Radioanal Nucl Ch 291:137–142

Riga-Karandinos AN, Saitanis CJ, Arapis G (2006) First study of anthropogenic platinum group elements in roadside top-soils in Athens, Greece. Water, Air and Soil Pollut 172:3–20

Rodrigues JM (2013) Evolução da frota de automóveis no Brasil, 2001-2012 (Relatório 2013), Instituto Nacional de Ciência e Tecnologia. Observatório das Metrópoles 2013:40p

Sen IS (2013) Platinum group element pollution is a growing concern in countries with developing economy. Environ Sci Technol 47(24):13903–13904

Schafer J, Puchelt H (1998) Platinum group metals (PGM) emitted from automobile catalytic converters and their distribution in roadside soils. J Geochem Explor 64:301–314

Sutherland RA, Pearson DG, Ottley CJ (2007) Platinum-group elements (Ir, Pd, Pt and Rh) in road-deposited sediments in two urban watersheds. Hawaii. Appl. Geochem. 22:1485–1501

Tomanik E (2000). Modelamento do desgaste por deslizamento em anéis de pistão em motores de combustão interna. PhD [Thesis]. Universidade de São Paulo, Brasil

Tsogas GZ, Giokas DL, Vlessidis AG, Aloupi M, Angelidis MO (2009) Survey of the distribution and time-dependent increase of platinum-group element accumulation along urban roads in Ioannina (NW Greece). Water Air Soil Pollut 201:265–281

Ward NI, Dudding LM (2004) Platinum emissions and levels in motorway dust samples: influence of traffic characteristics. Sci Total Environ 334–335:457–463

Wedepohl KH (1995) The composition of the continental crust. Geochim Cosmochim Acta 59:1217–1232

Wichmann H, Anquandah GAK, Schmidt C, Zachmann D, Bahadir MA (2007) Increase of platinum group element concentrations in soils and airborne dust in an urban area in Germany. Sci Total Environ 388:121–127

Whiteley JD, Murray F (2003) Anthropogenic platinum group element (Pt, Pd and Rh) concentrations in road dust and roadside soils from Perth, Western Australia. Sci Total Environ 317:121–135

Whiteley JD (2004) Autocatalyst derived platinum group elements in the roadside environment occurrence mobility and Fate PhD [Thesis]. Murdoch University, Australia

Whiteley JD (2005) Seasonal variability of platinum, palladium and rhodium (PGE) levels in road dusts and roadside soils, Perth, Western Australia. Water Air Soil Poll 160:77–93

Yajun W, Xiaozheng L (2012) Health risk of platinum group elements from automobile catalysts. Pro Eng 24:1004–1009

Yeomans AK, Golder AP (1982) The Guttman-Kaiser criterion as a predictor of the number of common factors. The Statistician 31:221–229

Zereini F, Wiseman C, Beyer JM, Artelt S, Urban H (2001) Platinum, lead and cerium concentrations of street particulate matter. J Soils Sediments 2(2):1–8

Zereini F, Alt F, Messerschmid TJ, Wiseman C, Feldmann I, Von Bohlen A, Muller J, Liebl K, Puttmann W (2005) Concentration and distribution of heavy metals in urban airborne particulate mater in Frankfurt am Main. Germany. Environ. Sci. Technol 39:2983–2989

Zereini F, Wiseman C, Putmann W (2007) Changes in palladium, platinum, and rhodium concentrations, and their spatial distribution in soils along a major highway in Germany from1994 to 2004. Environ Sci Technol 41:451–456

Zereini F, Wiseman CLS, Püttmann W (2012) In Vitro Investigations of Platinum, Palladium, and Rhodium Mobility in Urban Airborne Particulate Matter (PM_{10}, $PM_{2.5}$, and PM_1) Using Simulated Lung Fluids. Environ Sci Technol 46:10326–10333

Platinum, Palladium and Rhodium in a Bavarian Roadside Soil

Edzard Hangen and Thomas Dörr

Abstract As constituents of automobile exhaust catalysts platinum, palladium and rhodium are emitted by mechanical abrasion. Their deposition and vertical displacement in the soil was investigated along an east-west oriented transect at the Franken expressway (highway 73), Germany. With increasing distance to the road the concentrations of platinum, palladium and rhodium decreased exponentially. The influence of wind effects as well as of guard rails upon the lateral distribution of the three elements was clearly reflected. In view of a rising traffic density the pollution by platinum, palladium and rhodium becomes more important.

Keywords Platinum · Palladium · Rhodium · Roadside soils · Bavaria

1 Introduction

Automobile exhaust catalysts contain the transition metals platinum, palladium and rhodium, which belong to the platinum-group elements. Depending on the engine speed these are emitted by mechanical abrasion and deposited in roadside soils according to the volume of traffic and the topographical characteristics (Puchelt et al. 1995). Crop plants can show growth disturbances under increased soil concentrations (Abougalma 2004). While acute health hazards to humans caused by elevated contents of platinum, palladium and rhodium in the soil could not be observed until 2004 (Fritsche and Meisel 2004), airborne particular matter containing platinum, palladium and rhodium can bear adverse risk potential to human health (Wang and Li 2012). Against the background of a prospected increase in car

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traffic until 2030 (Shell Deutschland Oil GmbH 2009), further monitoring of the contents of platinum, palladium and rhodium in the soil becomes more significant. To supplement German measurement values, e.g. conducted in the states of Baden-Württemberg (Puchelt et al. 1995), Hesse (Zereini et al. 1997) and in the city of Braunschweig (Wichmann et al. 2007), by current data of Bavaria, investigations along roadside soils should be carried out. These should also address factors that influence the deposition onto soil such as the predominant wind direction or the combing-out effect of guard rails.

In a preliminary report the data of this article have been published (Hangen and Dörr 2010). The present publication has been permitted by the copyright holder.

2 Material and Methods

In cooperation with the Highway Maintenance Agency Erlangen the sampling position was determined at the highway 73, the so-called Franken expressway, at kilometer 149,341 (direction Nuremberg) (Fig. 1). Here, the lateral contaminant propagation is neither affected by embankments nor by trenches.

To estimate the emissions due to car traffic soil was sampled on the 3rd of April 2010 at both sides of the road at a distance of 0.5, 1.5 and 5 m to the roadside using an Nmin-auger according to Eckardt and Schäfer (1997). In the eastern direction in a distance of 2.25 m an additional spade sample was taken from underneath the guard rail to assess the combing-out- and the drip-zone effect upon the distribution of the mostly dust-transported transition metals. At the sampling points soil was sampled at 0–10 cm and 10–20 cm depth to consider the vertical displacement of platinum, palladium und rhodium.

Fig. 1 Sampling points at kilometer 149,341 (direction Nuremberg) at highway 73. The *arrow* is pointing towards the sampled transects; *left* East side; *right* West side. Adapted from Hangen and Dörr (2010), reprinted with copyright permission of the Municipality of Marktredwitz

Platinum, palladium und rhodium were analyzed in the aqua regia extract by IWW Rhenish-Westphalian Institute for Water, Mühlheim/Ruhr, Germany, using ICP-MS. Occurring interferences of rhodium were corrected mathematically, palladium was quantified after separation of the matrix using a highly acidic cation exchange column. Limits of determination amounted to 0.003 mg/kg for rhodium, 0.004 mg/kg for palladium, and 0.005 mg/kg for platinum, respectively. These limits of detection exceed those based on the laborious constriction using nickel sulfide-docimasy by a factor of 10 (Puchelt et al. 1995). In the evaluation all values < limit of determination were assigned half the value of determination (Hornung and Reed 1990).

3 Results and Discussion

With maximum concentrations of 0.086 mg/kg (Fig. 2a) and 0.023 mg/kg (Fig. 2c), respectively, platinum and rhodium contents in roadside soils along highway 73 are consistent with values of similar investigations. A comprehensive review (Rauch and Morrison 2008) amounts the concentration range in roadside soils for platinum at 0.025–0.25 mg/kg and for rhodium at 0.004–0.04 mg/kg, respectively. In contrast, the maximum palladium concentration of 0.047 mg/kg (Fig. 2b) along highway 73 markedly exceeds the maximum reference value of 0.012 mg/kg (Rauch and Morrison 2008). Opposite to platinum and rhodium, palladium was inserted into high temperature 3-way catalysts only after 1995 (Fritsche und Meisel 2004) and since then has been emitted and accumulated. Apparently, the data evaluation of Rauch and Morrison (2008) is based on earlier studies, which do not reflect the current palladium content of roadside soils.

With increasing distance to the roadside the contents of platinum, palladium and rhodium in the uppermost soil decreases almost exponentially (Fig. 2). This finding corresponds to other studies, (e.g., Puchelt et al. 1995) and might be attributed to the lateral distribution of coarse dust particles, which predominantly account for the sorption of platinum-group elements (Gao et al. 2012). For all three transition metals a distinct effect of the wind direction upon the contaminant's deposition and concentration in the soil becomes evident (Fig. 2). At the lee side, i.e. the east side of the road, the concentrations of platinum, palladium and rhodium in 5 cm soil depth reach the 1.6–2.5-fold value of the respective soil samples of the windward side, i.e. the west side.

In 15 cm soil depth the concentrations of the assessed contaminants are markedly lower as compared to those at the 5 cm soil depth (Fig. 2), what confirms the contaminants' input across the soil surface (Dikikh 2006). In a similar study the vertical transport velocity of platinum-group elements through urban soils was estimated to lie between 1.1 and 2.2 cm/y (Mihaljevič et al. 2013). Assuming an elevated input of platinum-group elements since 1993 (Wichmann et al. 2007), these velocities would lead to a vertical displacement between 18.7 and 37.4 cm soil depth until our sampling in 2010. This is in accordance with our findings. However, the palladium and rhodium contents in 15 cm soil depth fall mostly below the limit

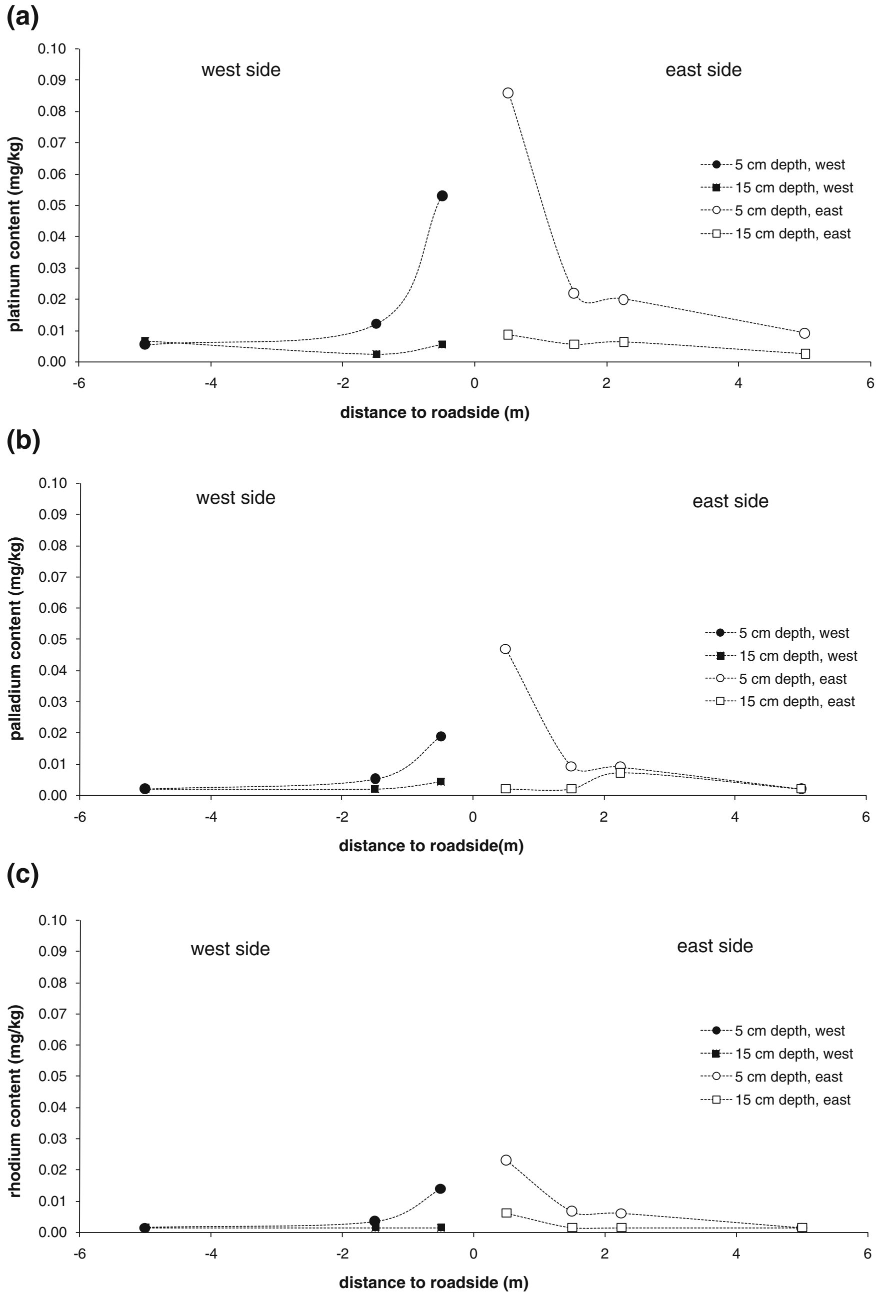

Fig. 2 **a** Platinum concentrations in roadside soils along highway 73. **b** Palladium concentrations in roadside soils along highway 73. **c** Rhodium concentrations in roadside soils along highway 73. Adapted from Hangen and Dörr (2010), reprinted with copyright permission of the Municipality of Marktredwitz

of determination (Fig. 2b, c). The sorption of platinum, palladium and rhodium to the soil matrix, which counteracts the vertical transport, is positively related to pH-value, content of humic substances, clay content and hydroxides (Dikikh 2006). For a number of soil horizons with pH-values <5 and different organic carbon contents, batch tests (48 h) with a liquid-solid ratio of 50:1 showed an increased sorption of palladium as compared to platinum (Abougalma 2004). This somewhat corresponds to our selective observations of vertical transport (Fig. 2a, b). However, in the batch tests rhodium showed a smaller sorptivity than platinum. In roadside soils along highway 73, rhodium was hardly detectable in 15 cm soil depth (Fig. 2b, c). This points to an intensified sorption in the topsoil or to an extensive rhodium transport underneath the sampled soil depth of 15 cm. The observed concentration ratio of platinum and rhodium contradicts the second hypothesis: The platinum-rhodium ratio of 3.7:1 found in the soil along highway 73 (Fig. 3) does not accord to that of the automobile exhaust catalysts, which conditional of manufacturing normally lies at 5:1 (Puchelt et al. 1995; Fritsche and Meisel 2004).

The closer platinum-rhodium ratio of our study might reflect the increased application of palladium-rhodium based catalysts after 1992 (Morcelli et al. 2005). Alternatively, the relatively higher solubility of rhodium (Zereini et al. 1997) or the mathematical correction of the interferences that occurred at the rhodium analysis could be responsible for the observed elevated rhodium concentrations.

Increased contaminant contents in 15 cm soil depth, 2.25 m east of the road, might reflect the combing-out- and the drip-zone effect of the guard rail (Puchelt et al. 1995) (Fig. 2a, b). Likely, coarse dust particles were deposited at the guard rail

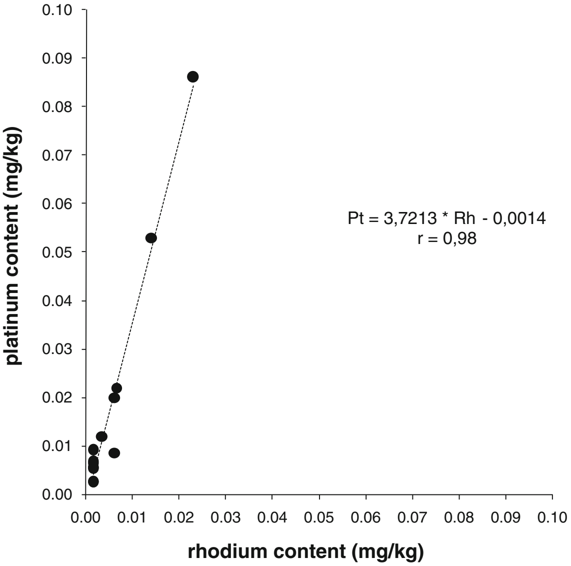

Fig. 3 Platinum- versus rhodium contents of the analyzed soil samples. Adapted from Hangen and Dörr (2010), reprinted with copyright permission of the Municipality of Marktredwitz

and due to the drip-zone effect markedly transported towards deeper soil depths during rain events. In contrast, contaminant contents in 5 cm underneath the guard rail do not show noticeable values. Here, due to the elevated infiltration of rain water in the drip-zone of the guard rail, the upper soil acts as a source rather than as a sink for contaminants (Fig. 2).

4 Conclusions

The first assessment of platinum, palladium and rhodium contents in roadside soils in Bavaria, Germany, displays the typical lateral distribution pattern and—apart from drip-zone effects—a small vertical contaminant transport. The soil concentrations reflect the increasing relevance of palladium in modern automobile exhaust catalysts. Additional soil samplings depending on traffic volume and engine load could further substantiate the contaminants' distribution in the soil, particularly because the environmental impact of platinum, palladium and rhodium will become more significant due to the rising traffic density and raising concerns over adverse health effects.

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References

Abougalma H (2004) Uptake, translocation, accumulation, and phytotoxicity of platinum group elements (PGE) on potato, lettuce, and barley. Dissertation, Karlsruhe University, 176 pp

Dikikh Y (2006) Adsorption und Mobilisierung wasserlöslicher Kfz-emittierter Platingruppenelemente (Pt, Rh, Pd) and verschiedenen bodentypischen Mineralen. *Karlsruher Mineralogische und Geochemische Hefte* 31, 125 pp

Eckhardt JD, Schäfer J (1997) PGE-Emissionen aus Kfz-Abgaskatalysatoren. In: Matschullat J, Tobschall HJ, Voigt HJ (eds) Geochemie und Umwelt: Relevante Prozesse in Atmo-, Pedo- und Hydrosphäre. Springer, Berlin, pp 181–188

Fritsche J, Meisel T (2004) Determination of anthropogenic input of Ru, Rh, Pd, Re, Os, Ir and Pt in soils along Austrian motorways by isotope dilution ICP-MS. Sci Total Environ 325:145–154

Gao B, Yu Y, Zhou H, Lu J (2012) Accumulation and distribution characteristics of platinum group elements in roadside dusts in Beijing, China. Environ Toxicol Chem 31:1231–1238

Hangen E, Dörr T (2010) Platin, Palladium und Rhodium in straßennahen Böden Bayerns. 6. Marktredwitzer Bodenschutztage, Municipality of Marktredwitz (ed), pp 161–166

Hornung RW, Reed LD (1990) Estimation of average concentration in the presence of nondetectable values. Appl Occup Environ Hyg 5:46–51

Mihaljevič M, Galušková I, Strnad L, Majer V (2013) Distribution of platinum group elements in urban soils, comparison of historically different large cities Prague and Ostrava, Czech Republic. J Geochem Explor 124:212–217

Morcelli CPR, Figueiredo AMG, Sarkis JES, Enzweiler J, Kakazu M, Sigolo JB (2005) PGEs and other traffic-related elements in roadside soils from Sao Paulo, Brazil. Sci Total Environ 345:81–91

Puchelt H, Eckhardt JD, Schäfer J (1995) Einträge von Platingruppenelementen (PGE) aus Kfz-Abgaskatalysatoren in straßennahe Böden. Landesanstalt für Umweltschutz Baden-Württemberg (eds), 15 pp

Rauch S, Morrison GM (2008) Environmental relevance of the platinum-group elements. Elements 4:259–263

Shell Deutschland Oil GmbH (2009) Shell Pkw-Szenarien bis 2030, 54 pp

Wang Y, Li X (2012) Health risk of platinum group elements from automobile catalysts. Procedia Eng 45:1004–1009

Wichmann H, Anquandah GAK, Schmidt C, Zachmann D, Bahadir AM (2007) Increase of platinum group element concentrations in soils and airborne dust in an urban area in Germany. Sci Total Environ 388:121–127

Zereini F, Skerstupp B, Alt F, Helmers E, Urban H (1997) Geochemical behaviour of platinum-group elements by automobile exhaust catalysts: experimental results and environmental investigations. Sci Total Environ 206:137–146

Increase of Platinum Group Element Concentrations in Soils and Airborne Dust During the Period of Vehicular Exhaust Catalysts Introduction

Hubertus Wichmann and Muefit Bahadir

Abstract In Europe, new cars had to be fitted with catalytic converters since 1993. Besides the desired air quality improvement, an accumulation of the catalytic active noble metals Pt, Pd, and Rh in the environment could soon be observed. This work aimed at a monitoring of platinum group element (PGE) emission and accumulation by comparing analytical data, all generated in 1999 and in 2005 and thus covering an important time span of vehicular exhaust catalysts introduction in Germany. A comparison of analytical results of 2005 with those of 1999 revealed a distinct increase of PGE concentrations in soils closely along heavy traffic roads mainly by a factor of 2–9 in the considered urban area located in northern Germany. At a crowded road in Braunschweig city with stop and go traffic, the highest soil concentrations were determined, namely 261 µg/kg for Pt, 124 µg/kg for Pd and 38.9 µg/kg for Rh. The investigations also revealed that especially Pt and Rh concentrations were comparably elevated in airborne dust in 2005. A sampling at the already mentioned roadside revealed airborne dust concentrations of 1,730 µg/kg for Pt, 410 µg/kg for Pd, and 110 µg/kg for Rh.

1 Introduction

Since 1993, all new cars sold in the European Union had to be fitted with catalytic converters. Undoubtedly, these measures brought about a great progress concerning traffic emission control. However, as it is common knowledge today, this technology also leads to new emissions (Moldovan 2007; Sobrova et al. 2012). A rapid accumulation of the catalytic active noble metals Pt, Pd, and Rh in the environment was observed and concerns arose about potential environmental and health risks (Wiseman and Zereini 2009; Wang and Li 2012). The investigation, briefly

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introduced in the following, aimed at contributing to the monitoring of platinum group element (PGE) emission and accumulation at an early stage. For this purpose, analytical data were gathered and compared, all generated in an urban area in Germany in 1999, when part of the vehicles with gasoline engines were already equipped with catalytic converters and in 2005, when almost all vehicles were carrying catalytic converters.

Oriented at the 1999 sampling strategy, soil and airborne dust samples were taken in 2005 at the same sampling sites located mainly close to heavily frequented roads in the city and the region of Braunschweig. For the enrichment of the analytes, conditioned soil samples as well as loaded glass fiber filters from air sampling were subjected to the nickel sulphide fire assay (also known as nickel sulphide docimasy). For the analyses, the ICP-MS technique was applied (Wichmann et al. 2007). For a better understanding of the results, some information about the course of the investigation is given first.

For this book contribution some text sections, tables and figures were adapted from (Wichmann et al. 2007, Sci. Total Envir. 388, 121–127) *with copyright permission of Elsevier Company* (2013).

2 Investigation Strategy

2.1 Sampling Sites

Investigations were carried out in Braunschweig, a town located in northern Germany with 240,000 inhabitants living on 192 km^2. Three major street sites were chosen for soil sampling based on traffic volume and driving style, which had not changed from the first to the second investigation period. Soils of the central area of the *City Park* were chosen to define the local background concentrations.

The *motorway B 248* links Braunschweig with another industrial city. About 16,000 vehicles per day were counted, moving in both directions. The motorway had a speed limit of 80 km/h. *Gifhorner Street* is a four-lane road between the center and an industrial area of Braunschweig. The vehicles ran on this road at about 50 km/h. About 230,000 cars and trucks passed this road daily.

Hagenring is another four-lane road that marks the eastern boundary of the city centre. Average speed on this road was about 40–60 km/h. Vehicular traffic was around 35,000 daily. Here, a constant speed was not observed due to the traffic lights close to the sampling sites. There was mainly stop and go traffic of vehicles. Airborne dust was also collected here, as described below.

2.2 Sampling and Preparation of Soils

Locations with fine-grained soils (<2 mm ∅) were selected for sampling. From each sampling site 4–6 soil cylinders of 10 cm height and 8 cm inner diameter were taken and separated into 0–2, 2–5 and 5–10 cm depth layers. The subsamples were pooled to get representative samples. In the laboratory, soil samples were dried at 105 °C and sieved through a mesh screen of 2 mm. A retain sample of 50 g was stored; another 50 g portion was subjected to the nickel sulphide fire assay.

2.3 Sampling of Airborne Dust

A high volume air sampler with a flow rate of 40 m^3/h and sampling inlet (PK 150–PU/G, according to VDI 1348, Riemer Messtechnik, Hausen, Germany) fitted with a glass fiber filter (diameter: 150 mm, particle size >0.5 µm, GF 8, Schleicher and Schuell) was used to collect airborne dust particles. Rauch et al. (2006) reported that PGE-containing particles emitted from automotive catalysts and present in air have diameters ranging from submicrometer to 63 µm, which is appropriate to the filter applied. The sampling inlet was placed 1 m above ground and 0.6 m alongside of *Hagenring Road*. Sampling was performed from 8 a.m. to 6 p.m. on workdays under dry weather conditions. Four filters were applied for an air volume of 2,691 m^3 and 246 mg of dry particulate matter was collected in total.

2.4 PGE Analysis

The PGE had to be enriched before detection. For this purpose, the nickel sulphide fire assay was applied (Wichmann and Bahadir 2001; Wichmann et al. 2007). To be used in the fire assay, the soil samples were weighed and kept at 640 °C for 2 h in order to decompose the organic matter. In order to prepare the glass fiber filters, they were just carefully torn.

The soil samples or torn glass fibre filters were given into glass bottles containing a collector consisting of nickel powder and sulphur as well as a flux mixture of sodium carbonate, sodium tetraborate, calcium fluoride and quartz sand. The mixture was poured into a chamotte fire clay crucible and heated to at least 1,160 °C. The crucible was removed after 1 h and allowed to cool down. During the process the PGE accumulated in the collector which separated as a button. The crucible was then broken and the button was mechanically separated from the silica slag.

The button was dissolved in HCl (37 %). The solution was allowed to cool down and the fine PGE particles were filtered off. The PGE containing residue was washed with diluted HCl and water in order to remove the dissolved green-coloured nickel sulphide. The residue was dissolved in a warm mixture of HCl (37 %) and H_2O_2 (30 %). The resulting solution was volume reduced by evaporation and filled up with diluted HCl to 10 mL for measurement. By this procedure, a pre-concentration of PGE as well as the removal of elements interfering the measurement were achieved.

The analyses were performed by ICP-MS. Indium was used as internal standard. The following masses were used: ^{103}Rh, ^{105}Pd, ^{106}Pd, ^{115}In, ^{194}Pt, ^{195}Pt. In order to avoid Ar interferences, the MS was equipped with a hydrogen rinsed gas collision cell. The instrumental detection limits (d.l.) were as follows [μg/kg]:

isotope	^{103}Rh	^{105}Pd	^{106}Pd	^{194}Pt	^{195}Pt
d.l.	0.02	0.03	0.03	0.015	0.02

Using soil samples and glass fiber filters spiked with PGE standard solutions as well as with solid Pt/Al_2O_3, the whole procedure was tested and the handling was optimized until recovery rates were ≥90 %. In the routine, spiked samples were analyzed periodically for continuous quality control.

3 Results and Discussion

3.1 PGE Concentrations in Soil

Samples from the *City Park* were taken from the central part of the area, at least 70 m away from a road. The following concentrations were found [μg/kg]: Pt: 1.10; Pd: 1.02; Rh: 0.10. These values are in the range of the mean concentrations in average shales (Govindaraju 1994). Therefore, the *City Park* values were defined as (local) background in this study. In few cases, the analyses of the roadside soil samples fell below the background values. These samples stem from greater distances from the road (>7.5 m) and from below 2 cm depth. Analytical results of the *Motorway B 248* sampling site are exemplarily listed in Table 1.

As can be seen from Table 1, the analytes could be detected in all the samples. Soil samples were taken right-angled to the main road in southern direction, whereas westerly winds prevail. PGE concentrations are typically highest close to the road and decline exponentially with increasing distance. These findings are principally in accordance with those determined by e.g. Fritsche and Meisel (2004). Regarding the top soil layer it is striking that especially Pt and Rh concentrations are found to be above background level at almost all sampling spots, indicating anthropogenic deposition up to 50 m away from the road. Measurements in 1999 revealed PGE concentrations above background level only in soil samples taken 0.1 m away from the *motorway B 248*. These are drawn for comparison purposes in Fig. 1.

At *motorway B 248* during the 6-year period PGE-concentrations increased by a factor of 3.7 for Pt, 6.5 for Pd, and 2.1 for Rh, respectively (Fig. 1). The decrease of concentrations in deeper soil layers, as exemplified in Fig. 2, was taken as an indication that the sampled soil layers were not seriously disturbed by human activities like repair measures for a considerable period of time.

Maximum PGE-concentrations as presented in Fig. 3, show the contamination situation at the *Gifhorner Street* in 1999 and 2005.

Table 1 PGE concentrations in soil samples collected at *motorway B 248*

Distance from motorway (m)	Depth (cm)	Rh (µg/kg)	Pd (µg/kg)	Pt (µg/kg)
0.1	0–2	10.7	43.3	50.4
	2–5	5.98	14.4	29.5
2.5	0–2	4.45	17.6	19.3
	2–5	1.82	7.59	9.10
5.0	0–2	1.10	3.18	4.90
	2–5	0.66	1.20	2.90
7.5	0–2	0.24	2.05	1.60
	2–5	0.15	0.54	1.20
10	0–2	0.29	0.89	2.10
	2–5	0.13	0.46	1.89
20	0–2	0.29	2.43	1.30
	2–5	0.20	1.49	0.10
50	0–2	0.18	0.90	4.00
	2–5	0.17	1.29	0.10

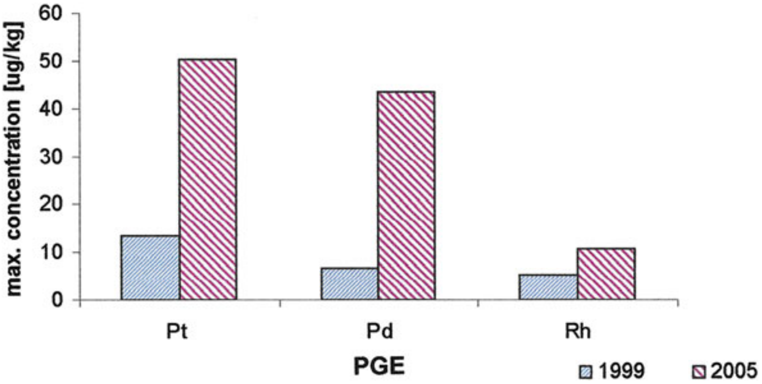

Fig. 1 Comparison of PGE concentrations at *motorway B 248* in soil samples taken in 1999 and 2005 (distance: 0.1 m; *top* soil). Adapted from (Wichmann et al. 2007, Sci. Total Envir. 338, 121–127). Reprinted with copyright permission, Elsevier

In 2005 as well as in 1999, highest concentrations of Pt, Pd, and Rh were detected in soils at the narrow center strip of this sampling site. The center strip is closely located to all four lanes of the road and thus, compared to the roadside, twice the amount of vehicles run close to it. Indeed, twice the concentration could be determined there for all three PGEs compared to the sampling spot located directly at the roadside. Just within 6 years, the concentrations raised by factor of 2.1 for Pt, 8.9 for Pd, and 2.8 for Rh (Fig. 3).

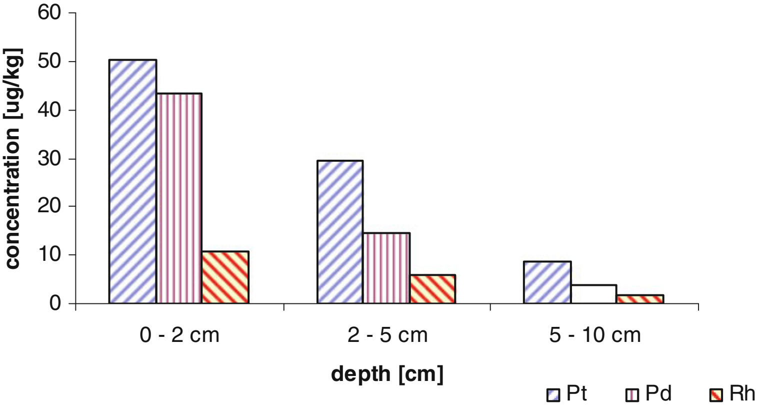

Fig. 2 PGE concentrations at 0.1 m away from *motorway B 248* versus depth of soil. Adapted from (Wichmann et al. 2007, Sci. Total Envir. 338, 121–127). Reprinted with copyright permission, Elsevier

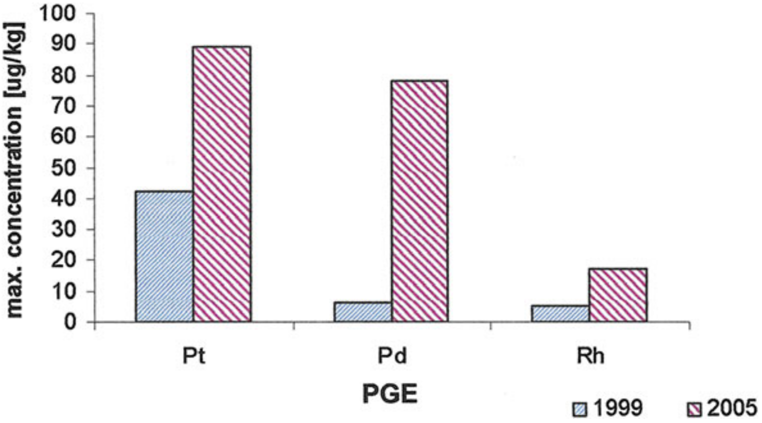

Fig. 3 Comparison of PGE concentrations at the *Gifhorner Street* in soil samples taken in 1999 and 2005 (center strip, *top* soil). Adapted from (Wichmann et al. 2007, Sci. Total Envir. 338, 121–127). Reprinted with copyright permission, Elsevier

At the *Hagenring*, PGE contamination was found to be highest at the northern roadside sampling site. These analytical results are depicted in Fig. 4.

Compared with all other sampling sites, highest amounts of Pt, Pd, and Rh could be detected in the top soil layer at the *Hagenring* (compare Figs. 1, 3 and 4). Of course, PGE accumulation is influenced by the daily volume of traffic and by the driving style. Especially during the rush hours, vehicles are stopped up to the northern *Hagenring* sampling spot by the traffic lights. This stop and go effect is known to raise PGE emissions (Morcelli et al. 2005). The increase of Pt, Pd, and Rh concentrations at this site within 6 years were by factors of 7.3, 15, and 6.6, respectively (Fig. 4).

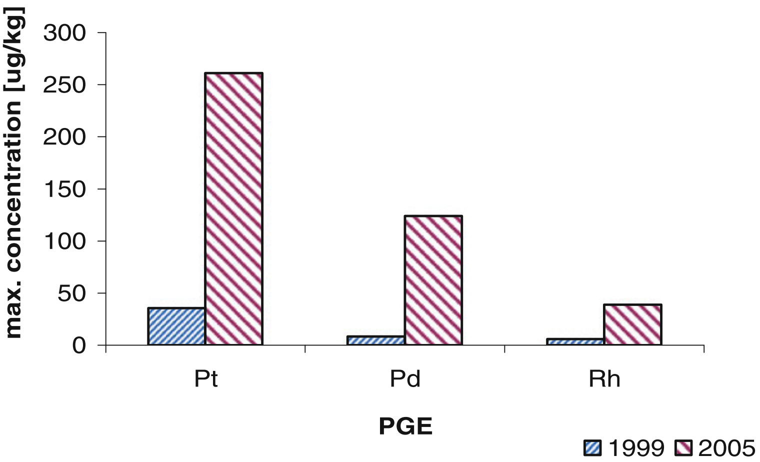

Fig. 4 Comparison of PGE concentrations at *Hagenring* in soil samples taken in 1999 and 2005 (distance: 0.1 m; *top* soil). Adapted from (Wichmann et al. 2007, Sci. Total Envir. 338, 121–127). Reprinted with copyright permission, Elsevier

3.2 PGE Contamination of Air and Airborne Dust

As described in Sect. 2.3, collection of airborne dust was performed with a high volume sampler located at the northern roadside of the *Hagenring*. The PGE-concentrations and the data from 1999 are compiled in Table 2 for comparison purposes.

The PGE-concentrations of 2005 lie within concentration ranges found in similar studies (Puls et al. 2012; Rauch et al. 2006; Zereini et al. 2004): 0.9–246 pg/m^3 for Pt, 0.1–44 pg/m^3 for Pd, and 0.2–15 pg/m^3 for Rh. The same conformity with literature data was found in 1999, as well (Wichmann and Bahadir 2001). Apparently, PGE concentrations in airborne solid matter are distinctly higher in 2005 than in 1999 for Pt and Rh (Table 2). While the Pd-concentration was highest in 1999, Pt clearly dominated in 2005. In 1999 there was an increased application of Pd as compared to Pt in exhaust catalysts. The total PGE emission was lower because the majority of the cars and especially the diesel-powered automobiles and lorries were

Table 2 PGE concentrations of air and airborne dust sampled in 2005 and 1999 at the *Hagenring* in Braunschweig, Germany

PGE	1999		2005	
	Air (pg/m^3)	Dust (µg/kg)	Air (pg/m^3)	Dust (µg/kg)
Pt	6.0	67	159	1,730
Pd	33.9	375	37.8	410
Rh	1.2	13	10.0	110

not equipped with catalytic converters which were based on PGE. When comparing PGE-concentrations in air and dust with those in soils, it has to be kept in mind that the first represent a snapshot of the condition during air sampling whereas the second comprise long-term accumulation.

4 Conclusion

A comparison of the 1999 and 2005 contamination situation concerning the noble metals Pt, Pd, and Rh at identical sampling spots in an urban area in northern Germany was carried out. A distinct increase of PGE concentrations by a factor of 2.1 to a factor of 8.9, singularly even to a factor of 15, was determined in soils close to heavy-traffic roads. Furthermore, elevated Pt and Rh concentrations were found in airborne dust.

The wide range of increase in PGE concentration can surely be attributed to different environmental influences upon the top soils at the sampling spots during 6 years time, but also to technical reasons concerning variations in catalytic converter construction and varying PGE combinations. An ongoing accumulation of the quite immobile PGE in soil and road dust is still expected. Therefore, a widespread monitoring has to be continued.

References

Fritsche J, Meisel T (2004) Determination of anthropogenic input of Ru, Rh, Pd, Re, Os, Ir, and Pt in soil along Austrian motorways by isotope dilution ICP-MS. Sci Total Environ 325:145–154

Govindaraju K (1994) Compilation of working values and sample description for 383 geostandards. Geostan Newsl 18:1–158

Moldovan M (2007) Origin and fate of platinum group elements in the environment. Anal Bioanal Chem 388:537–540

Morcelli CPR, Figueiredo AMG, Sarkis JES, Enzweiler J, Kakazu M, Sigolo JB (2005) PGEs and other traffic-related elements in roadside soils from Sao Paulo, Brazil. Sci Total Environ 345:81–91

Puls C, Limbeck A, Hann S (2012) Bioaccessibility of palladium and platinum in urban aerosol particulates. Atmos Environ 55:213–219

Rauch S, Peucker-Ehrenbrink B, Molina LT, Molina MJ, Ramos R, Hemond HF (2006) Platinum group elements in airborne particles in Mexico City. Environ Sci Technol 40:7554–7560

Sobrova P, Zehnalek J, Adam V, Beklova M, Kizek R (2012) The effects on soil/water/plant/animal systems by platinum group elements. Cent Eur J Chem 10:1369–1382

Wang Y, Li X (2012) Health risk of platinum group elements from automobile catalysts. Proc Eng 45:1004–1009

Wichmann H, Anquandah GAK, Schmidt C, Zachmann D, Bahadir AM (2007) Increase of platinum group element concentrations in soils and airborne dust in an urban area in Germany. Sci Total Environ 388:121–127

Wichmann H, Bahadir M (2001) Determination of the noble metals platinum, rhodium, and palladium in airborne particles. Fresenius Environ Bull 10:106–108

Wiseman CLS, Zereini F (2009) Airborne particulate matter, platinum group elements and human health: a review of recent evidence. Sci Total Environ 407:2493–2500

Zereini F, Alt F, Messerschmidt J, von Bohlen A, Liebl K, Püttmann W (2004) Concentration and distribution of platinum group elements (Pt, Pd, Rh) in airborne particulate matter in Frankfurt am Main Germany. Environ Sci Technol 38:1686–1692

Platinum-Group Elements in Urban Fluvial Bed Sediments—Hawaii

Ross A. Sutherland, Graham D. Pearson, Chris J. Ottley and Alan D. Ziegler

Abstract Results from a detailed examination of the abundance, spatial variability and grain-size fractionation of platinum-group elements (PGEs; iridium, Ir; palladium, Pd; platinum, Pt; and rhodium, Rh) in bed sediments of an urban stream in Honolulu (Hawaii, USA) indicate significant contamination of Pd, Pt, and Rh. PGE concentrations in sediments located in close proximity to storm drains followed the sequence of Pt (10.3–24.5 ng g^{-1}) > Pd (5.9–12.6 ng g^{-1}) > Rh (0.82–2.85 ng g^{-1}) > Ir (0.11–0.23 ng g^{-1}). From a contamination perspective, enrichment ratios followed the sequence of Rh (25.3) ≫ Pd (6.9) = Pt (6.8) ≫ Ir (2.3). Iridium was primarily geogenic in origin, while the remaining PGEs indicated significant anthropogenic contamination. Attrition of the PGE-loaded three-way catalytic converters and their release to the road environment is the most likely source of PGEs in the stream sediments examined. PGE enrichment of bed sediments likely resulted from direct transport of sediment-associated road runoff via storm drains. Preliminary work on grain-size partitioning showed preferential enrichment and mass loading of Pd, Pt, and Rh in grain-size fractions ranging from 63 to 1,000 μm. Data from this study have direct implications for contaminant transport, and sediment source identification in urban catchments. Rhodium, in particular, emerged as an element potentially useful for sediment fingerprinting.

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Environmental Science and Engineering, DOI 10.1007/978-3-662-44559-4_12

1 Introduction

Platinum-group elements (PGEs) Pd, Pt, and Rh, are incorporated in three-way catalysts (TWCs) to reduce vehicle emissions. These noble metals promote three main reactions: reduction of nitrous oxides to N and H_2O, oxidation of CO to CO_2, and final combustion (oxidation) of residual hydrocarbons (Lucena et al. 1999). Three-way catalyst systems destroy more than 90 % of engine emissions (Acres and Harrison 2004). Since the mandatory use of catalytic converters in new gasoline automobiles in the UK (1993), substantial health benefits have accrued (Hutchinson and Pearson 2004). The estimated net societal health benefits by 1998 were approximately £500 million, and by 2005 they were estimated at £2 billion.

Countering their importance in reducing automobile-related atmospheric contamination, is the concern the PGEs are released to the road environment and atmosphere in exhaust emissions following TWC wear/attrition (Ravindra et al. 2004; Kalavrouziotis and Koukoulakis 2009; Wiseman and Zereini 2009). Modern manufacturing processes produce catalytic converter washcoats covered in PGE particles of 0.3 μm down to nanoparticle sizes (Prichard and Fisher 2012). Alumina is commonly employed as a high surface area support for washcoats and act as a carrier for dispersed PGEs, CeO_2-ZrO_2 mixed oxides, and barium and/or lanthana oxides (Kaspar et al. 2003). Fragments of TWC have been found in the road-deposited sediments of London and Sheffield, U.K., with sizes of 25 μm and between 40 and 80 μm covered in minute PGE particles (<0.3 μm). Dynamometer studies have indicated automotive outputs of PGEs to the environment are typically only tens to hundreds of ng km^{-1} (Palacios et al. 2000). However, low emission rates of PGEs are greatly magnified by the large vehicle numbers in urban environments. The introduction of PGEs to the environment from vehicles is therefore significant—particularly when considering that the concentrations of PGEs in bedrock are typically at the ultra-trace level: Ir, Pd, Pt, and Rh are 0.05, 0.4, 0.4, and 0.06 ng g^{-1}, respectively (continental crust; Wedepohl 1995).

In addition to localized deposition of PGEs on road surfaces (Ely et al. 2001; Zereini et al. 2001; Sutherland et al. 2007; Mathur et al. 2011; Spada et al. 2012), roadside soils (Morton et al. 2001; Whiteley and Murray 2003; Marcheselli et al. 2010; Akrivi et al. 2012; Lee et al. 2012), and roadside vegetation (Djingova et al. 2003; Riga-Karandinos and Saitanis 2004; Pan et al. 2009; Fumagalli et al. 2010), there is increasing evidence of deposition in a variety of sedimentary sinks following particle-associated transport of PGEs throughout urban catchments (Tuit et al. 2000; Rauch et al. 2004; Jackson et al. 2007; Pratt and Lottermoser 2007; Prichard et al. 2008). Early PGE research in Sweden by Wei and Morrison (1994a, b) found Pt to accumulate in roadside 'gullypots' and in downstream sediments. More recently, PGE concentrations, well above background levels, have been found in a roadside detention basin in England (de Vos et al. 2002), and in stormwater infiltration basins in Australia (Whiteley and Murray 2005).

To date, only limited research has focused on quantifying the abundance of PGEs in fluvial bed sediments receiving direct runoff from urban watersheds (e.g., Jackson et al. 2007; Prichard et al. 2008). This is surprising given the ability of PGEs to bioaccumulate (Ek et al. 2004; Zimmermann et al. 2005 Nischkauer et al. 2013; Wren and Gagnon 2014), as well as their significant environmental solubility and bioavailability (Jarvis et al. 2001; Fliegel et al. 2004; Colombo et al. 2008a, b; Puls et al. 2012).

The aims of this paper are to present results of a baseline survey of PGE concentrations (Ir, Pd, Pt and Rh) and enrichment ratios in fluvial bed sediments in an urban Hawaiian stream impacted by direct road runoff via storm drains. Our working hypothesis was that anthropogenic enrichment of PGEs, if present, would be associated with road sources. We also examined the distribution of PGEs within a range of grain size fractions to test the commonly held notion that elements are often found most in abundance in small grain-size fractions.

2 Experimental

2.1 Study Area

Nuuanu catchment (11.7 km^2), located in Honolulu, Hawaii (USA) was the subject of a prior investigation on automotive-associated Cu, Pb and Zn contamination (Andrews and Sutherland 2004), and PGEs in road-deposited sediments (RDS) (Sutherland et al. 2008). The catchment is situated on the southern side of the Koolau Volcanic range on the island of Oahu. Much of the valley is now covered with layers of alluvium and soil. The underlying geology consists of basaltic lavas.

Nuuanu Valley is one of the oldest developed valleys on Oahu. Fifty-one percent of the surface area in catchment is forested conservation land, and 49 % is developed. Developed land in the lower catchment consists of: manufacturing/industry (6 %), commercial (~9 %), social services (9 %), open space (14 %), public infrastructure (16 %), and residential (46 %) (Steve Anthony, US Geological Survey, personal communication, 2002). The population density in the catchment is 1,287 persons per km^2 (Brasher and Anthony 2000). Daily traffic volumes on streets range from 3,440 to 19,500 vehicles per 24 h, with highway counts between 37,800 and 46,000.

2.2 Sample Collection and Processing

Bed sediment samples were collected in 2002 at seven storm drains in Nuuanu Stream under baseflow conditions (see Fig. 1 in Andrews and Sutherland 2004). Archived samples from three of these sites have been reexamined for the present study (Judd, Vineyard and Beretania). Sampling locations were selected based on access, the presence of sediment deposition zones, and a direct and obvious connection from the road inlet to the storm drain outlet into Nuuanu Stream. The Judd Street outlet primarily drains residential areas and has the lowest traffic densities.

Vineyard and Beretania Street outlets are closer to the mouth of Nuuanu Stream and Honolulu Harbor; and they drain mostly commercial land uses and have high traffic densities. To explore spatial patterns in PGE abundance, bed sediment samples were collected at the drain outlet (0 m) and 5, 10, and 20 m above, and below the outlet. Three baseline bed sediment samples were collected in a remote but accessible unnamed small tributary to Nuuanu Stream, located in headwaters of the catchment. At all sampling locations, six cores were extracted from the stream bed with an acid-washed plastic cylinder to a depth of 5 cm, and then composited.

Samples were oven-dried in the laboratory at 105 °C to a constant mass. Dried samples were gently disaggregated and passed through a 2-mm stainless steel sieve. The material retained on the 2-mm sieve was discarded. All material passing the 2-mm sieve was further sieved with a <63 μm stainless steel sieve for 10-min on a Ro-Tap shaker (W.S. Tyler, Mentor OH). The <63 μm size fraction was retained for analysis, as this is the most commonly measured size range in environmental contamination studies dealing with soil and sediment (e.g., Radakovitch et al. 2008; Aleksander-Kwaterczak and Helios-Rybicka 2009; Milacic et al. 2010; Owens et al. 2011; Akrivi et al. 2012; Gao et al. 2012, 2014; Saeedi et al. 2013). Material retained on the 63 μm sieve for the Vineyard storm drain outlet (0 m) sample was further fractionated using a 'nest' of stainless steel sieves. The mass in each of the grain size fractions was determined to a precision of ±0.001 g. The six fractions retained for PGE analysis and their sedimentological equivalents in parentheses were: <63 μm (silt and clay), 63–125 μm (very fine sand), 125–250 μm (fine sand), 250–500 μm (medium sand), 500–1,000 μm (coarse sand), and 1,000–2,000 μm (very coarse sand). Samples >63 μm were ground in tungsten carbide vials, with tungsten carbide balls to enhance homogeneity during digestions. All material was subsequently passed through a 63-μm nylon mesh screen.

2.3 Chemical Analyses and Quality Control

Details of the analytical methods are reported elsewhere (Sutherland et al. 2007). Briefly, samples weighing 100 mg were placed in sealed Teflon vials and digested at 180 °C with aqua regia (3:1 volumetric ratio of HCl and HNO_3) for 48 h. The solution was taken to dryness and re-dissolved in 6 N HCl, dried again and taken up in 2 mL of 0.5 N HCl. This solution was centrifuged and loaded onto a chromatography column containing 2 mL of pre-cleaned AG50-X8 200-400# cation exchange resin (Bio-Rad Laboratories, Hercules, CA).

Column yields for Ir, Pd, Pt and Rh varied between 98.8 and 101.2 % (n = 4). Column blanks were <1 pg for Ir, 1 pg Rh, 6 pg for Pd and 10 pg for Pt. Total analytical blanks were routinely 6 pg for Ir, 10 pg for Rh, 13 pg for Pd and 30 pg for Pt. Procedural detection limits were <10 pg g^{-1} for Ir, 10 pg g^{-1} for Rh and <30 pg g^{-1} for Pd and Pt.

Samples were analyzed at the Department of Earth Sciences (Durham University) on a Perkin Elmer Sciex Elan 6000 (Wellesley, MA) inductively coupled plasma-mass spectrometer (ICP-MS) equipped with a CETAC Aridus desolvating nebulizer (Omaha, NE). The following isotopes ^{103}Rh, ^{105}Pd, ^{191}Ir, and ^{195}Pt were used for quantification of elemental abundances.

Oxides of concern during the analysis of environmental samples contaminated by catalytic converter products include ^{87}Sr^{16}O, ^{86}Sr^{17}O and ^{89}Y^{16}O, as they interfere with the determination of ^{103}Rh and ^{105}Pd. The oxides of Sr and Y were quantitatively retained by the cation column relative to PGEs, thus effectively separating them and causing minimal interference problems (Sutherland et al. 2007). In addition, on-line correction was also conducted for these species in case that there may have been inefficient separation. Interference from isobaric oxides of Hf (^{179}Hf^{16}O) and Zr (^{90}Zr^{16}O) was greatly reduced by using the desolvating nebulizer. Therefore oxide generation levels were maintained at or below 0.05 % of the total metal signal, and these were readily corrected from PGE analyte signals (Sutherland et al. 2007).

Classical precision and accuracy were measured with the BCR-723 certified reference material, which is a tunnel dust sample (Zischka et al. 2002a, b). This is the only available environmental reference material with certified PGE concentrations for selected elements. Mean certified concentrations (±standard deviation) in BCR-723 are: Pd, 6.0 ± 2.19 ng g^{-1}; Pt, 81.3 ± 4.60 ng g^{-1}; and Rh, 12.8 ± 1.59 ng g^{-1}. Four independent dissolutions of BCR-723 were performed using the methods previously described. Precision for Pd, Pt, and Rh ranged from 2 to 6 %. Precision was lower for Ir, but still acceptable at 12 % given the ultra-trace concentrations (0.29 ± 0.036 ng g^{-1}). Accuracy for Pt and Rh were +3 % and −7 %, respectively. The accuracy for Pd was −25 %, but the concentration of 4.47 ± 0.26 ng g^{-1} was statistically the same as that measured for BCR-723 by Meisel et al. (2003) using isotope dilution ICP-MS following a HCl and HNO_3 digestion (i.e., 4.52 ± 0.23 ng g^{-1}). Sutherland (2007) questioned the veracity of the certified value of Pd in BCR-723, as 7 of the 48 values used in the certification process had values ≥ 10.1 ng g^{-1}. Following removal of these potential outliers, the median Pd value for BCR-723 becomes 4.9 ng g^{-1}, similar to that determined by Kanitsar et al. (2003). Accuracy could not be determined for Ir as this element is not certified in BCR-723. However, our data agree closely with the mean value of 0.26 ± 0.047 ng g^{-1} determined by Meisel et al. (2003) after removal of an extreme outlier.

2.4 PGE Enrichment Ratios and Grain-Size Fractionation

Grain-size normalized enrichment ratios (ERs) were computed to evaluate the level of contamination:

$$\mathrm{ER_{PGE}} = \frac{\mathrm{C_{PGE}\ Sample}}{\mathrm{C_{PGE}\ Baseline}}$$

where, ‘C’ represents the concentration of a given PGE in either a storm-drain associated bed sediment sample, or the mean (n = 3) baseline value determined for sediments in a remote area of Nuuanu catchment.

A preliminary examination of the total element loading ($\mathrm{GSF_{Load}}$) for one outlet stream sediment sample (Vineyard, 0 m) was determined using concentration data for each of the six grain-size fractions with their mass grain size percentages (Sutherland 2003; Sutherland et al. 2008):

$$\mathrm{GSF_{Load}} = \left[\frac{\mathrm{Pt_i} \bullet \mathrm{GS_i}}{\sum_{n=i}^{6} \mathrm{Pt_i} \bullet \mathrm{GS_i}}\right] \bullet 100$$

where in this example, $\mathrm{Pt_i}$ is the platinum concentration in an individual grain-size fraction (e.g., <63 μm) in $\mathrm{ng\ g^{-1}}$; and $\mathrm{GS_i}$ is the mass percentage of an individual fraction (0–100 %).

3 Results and Discussion

3.1 Baseline PGE Concentrations

The bed sediment samples in the headwaters of Nuuanu catchment had the following mean concentrations (±1 SD): Ir = 0.080 ± 0.00 $\mathrm{ng\ g^{-1}}$, Pd = 1.39 ± 0.20 $\mathrm{ng\ g^{-1}}$, Pt = 2.49 ± 0.18 $\mathrm{ng\ g^{-1}}$, and Rh = 0.067 ± 0.006 $\mathrm{ng\ g^{-1}}$. These data are comparable to those for three baseline soil samples, analyzed using the sample methodology, in a nearby catchment (Sutherland et al. 2007): Ir = 0.095 ± 0.010 $\mathrm{ng\ g^{-1}}$, Pd = 1.12 ± 0.19 $\mathrm{ng\ g^{-1}}$, Pt = 1.98 ± 0.63 $\mathrm{ng\ g^{-1}}$, and Rh = 0.070 ± 0.014 $\mathrm{ng\ g^{-1}}$. The baseline Pd and Pt values from Nuuanu catchment bed sediments are substantially greater than the 0.4 $\mathrm{ng\ g^{-1}}$ values associated with data for the continental crust compiled by Wedepohl (1995) from European greywackes, or the values from Chinese loess, representing upper continental crust, determined by Park et al. (2012), with Pt and Pd concentrations of 0.60 and 0.53 $\mathrm{ng\ g^{-1}}$, respectively. The significantly higher Pd and Pt abundances in Hawaii reflect the dominance of basalt in the islands versus this igneous rock’s proportion in the continental crust.

Baseline Ir concentration data from this study are similar to the 1919 basaltic flow on the island of Hawaii (BHVO-1), and the tholeiites from Kohala Volcano (Table 1). They are also significantly lower than the tholeiite basalts from Kilauea, and Mauna Loa Volcanoes. Palladium and Pt baseline data were most similar to those for tholeiites analyzed by Tatsumi et al. (1999) and Crocket (2000). Baseline Rh data are similar to those for BHVO-1, as Meisel and Moser (2004) report Rh concentrations ranging from 0.054 to 0.27 $\mathrm{ng\ g^{-1}}$.

Table 1 Summary of average (±SD) PGE concentrations (ng g^{-1}) in geologic materials from Hawaii

Geologic material	No.	Ir	Pd	Pt	Rh
Picrites[a]	10		3.41 ± 2.32	4.10 ± 1.32	
Unaltered tholeiites[b]	18	0.376 ± 0.140		2.40 ± 1.04	
BHVO-1[c]	5	0.085 ± 0.018	3.06 ± 0.074	3.08 ± 0.99	0.113 ± 0.091
BHVO-1[d]	5	0.096 ± 0.012	2.86 ± 0.18	2.42 ± 0.42	
Koolau Volcano glass[e]	13			5.08 ± 1.71	
Tholeiites (Mauna Loa)[f]	4	0.289 ± 0.060	1.94 ± 0.26	3.13 ± 0.71	0.154 ± 0.046
Tholeiites (Kilauea)[f]	5	0.418 ± 0.046	2.10 ± 0.22	2.55 ± 0.29	0.152 ± 0.033
Tholeiites (Kohala)[g]	7	0.100 ± 0.085		2.66 ± 1.34	
Tholeiites (Kilauea Iki Lava Lake)[h]	32	0.296 ± 0.243	2.78 ± 1.94	4.29 ± 6.78	<0.5

[a] Bennett et al. (2000), includes Kilauea (3), Loihi (2), Mauna Kea (1), Hualalai (1), Mauna Loa (1) and Koolau (2)

[b] Crocket (2000), includes Kilauea Summit (4), Kilauea East Rift (12), and Hilina Pali (2)

[c] BHVO-1 basaltic *pahoehoe* lava from the Hawaii Volcano Observatory that overflowed from the Halemaumau crater in 1919. BHVO-1 is a US Geological Survey reference material (*minerals.cr.usgs.gov/geo_chem_stand/pdfs/basalt**bhvo**2.pdf*). Data from Meisel and Moser (2004)

[d] Data from Peucker-Ehrenbrink et al. (2003)

[e] Data from Norman et al. (2004)

[f] Data from Tatsumi et al. (1999)

[g] Data from Jamais et al. (2008), shield-building stage, Pololu Volcanics

[h] Data from Pitcher et al. (2009), olivene-rich lava formed during 1959 summit eruption of Kilauea Volcano

3.2 Storm-Drain Associated Bed Sediment PGE Concentrations

Mean PGE concentrations in the <63 μm fraction follow the sequence (Table 2): Pt (17 ng g^{-1}) > Pd (10 ng g^{-1}) > Rh (1.7 ng g^{-1}) > Ir (0.18 ng g^{-1}). Palladium, Pt and Rh concentrations in storm-drain associated bed sediments exceed baseline values for Nuuanu catchment (Fig. 1). The range of concentrations in the bed sediments for Pd, Pt and Rh are less than those found in Nuuanu Valley road-deposited sediments (Sutherland et al. 2008). Moreover, the mean bed sediment concentrations were significantly lower (unpaired t-test) than those in RDS for Pd (P-value = 0.010), Pt (P-value = 0.006), and Rh (P-value = 0.005). There was no significant difference between Ir concentrations in road and bed sediments (P-value = 0.57). The consistently greater concentrations of Pd, Pt and Rh in road sediments versus bed sediments suggests dilution of PGE contaminated road sediment delivered to the stream via storm drains, with sediments from the less-developed headwater areas of Nuuanu catchment.

There are some data to support the dilution of autocatalyst-associated PGEs along sediment transport pathways in urban watersheds. For example, the average

Table 2 Platinum-group element concentrations (ng g^{-1}) in the <63 μm grain size fraction of bed sediments from Nuuanu Stream, Oahu, Hawaii (n = 21)

Statistic[a]	Ir	Pd	Pt	Rh
Mean ± SD	0.18 ± 0.063	9.67 ± 5.14	16.9 ± 9.6	1.69 ± 1.05
CV (%)	35.1	53.2	56.9	62.4
Minimum	0.080	3.16	5.76	0.32
Maximum	0.28	20.5	40.2	3.46
25th percentile	0.12	5.68	9.06	1.04
Median	0.18	8.44	15.1	1.35
75th percentile	0.24	13.6	24.1	2.71

[a] SD is the standard deviation and CV is the coefficient of variation

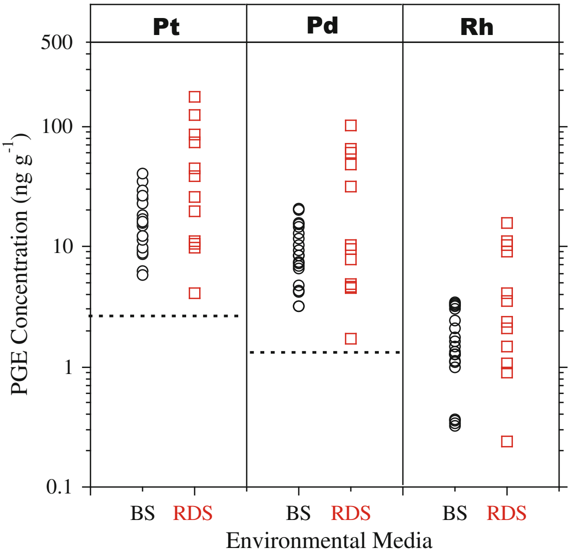


Fig. 1 Concentrations of Pt, Pd and Rh in the <63 μm fraction of 21 bed sediment (BS) samples and 12 road-deposited sediments (RDS) from Nuuanu watershed. The RDS data are from Sutherland et al. (2008). Note the *horizontal dotted line* across the Pt and Pd 'panels' represent the average baseline concentrations for Nuuanu watershed, 2.5 ng g^{-1} and 1.4 ng g^{-1}, respectively. The baseline value for Rh (0.07 ng g^{-1}) is less than the minimum value on the y-axis and is not plotted

Pt concentrations in roadside 'gullypot' sediments in Goteborg, Sweden (7.1 ± 4.0 ng g^{-1}), measured by Wei and Morrison (1994a), were higher than the bed sediment Pt concentrations in nearby rivers (<0.5–2.2 ng g^{-1}) (Wei and Morrison 1994b). Concentrations of Pd, Pt, and Rh in a sediment retention basin associated with the M20 motorway in England were significantly higher than those in the nearby River Stour, Kent (de Vos et al. 2002). Available PGE data for RDSs reported by Whiteley and Murray (2003), for West Coast and Leach Highways in Perth, Australia, were combined with those reported for stormwater infiltration basins in the same locations (Whiteley and Murray 2005). These data indicate that road sediments had higher PGE concentrations than those 'downstream' in the infiltration basins. For example, Pt, Pd, and Rh concentrations were 1.9–2.9 times, 2.6–5.4 times, and 2.4–3.3 times greater in RDS, respectively. Finally, data from Prichard et al. (2008) indicate an order of magnitude greater concentration of Pd, Pt, and Rh in RDS in Coisley Hill, Sheffield compared to bed sediments in the nearby Shire Brook.

3.3 Spatial Variation in Bed Sediment Concentrations About Storm Drain Outlets

Bed sediment data from three storm drains (Judd, Vineyard and Beretania Streets) were examined in detail to determine the effect of location on PGE contamination near drains (Table 3). Results from the Kruskal-Wallis test (Zar 1996) indicated at least one significant pair-wise difference for Pd (P-value = 0.0027), Pt (P-value = 0.0067), and for Rh (P-value = 0.0021). Pair-wise comparisons (Mann-Whitney U-test followed by a Bonferroni correction) indicated sediments associated with the furthest upstream storm drain outlet (Judd St.) had the lowest concentrations of Pd (5.9 ng g^{-1}), Pt (10.3 ng g^{-1}) and Rh (0.8 ng g^{-1}). Iridium concentrations were highest in Judd (0.23 ng g^{-1}) and Vineyard (0.20 ng g^{-1}) bed sediments. Similarity in data for two very different locations support the notion that traffic and land use had limited influence on the spatial distribution of Ir in the bed sediments of this system.

Conversely, Vineyard bed sediment-associated concentrations of Pd (12.6 ng g^{-1}), Pt (24.5 ng g^{-1}), and Rh (2.9 ng g^{-1}) were significantly greater than

Table 3 Mean ± SD (median in parentheses) for PGE concentrations (ng g^{-1}) in the <63 μm grain size fraction of bed sediments associated with three storm drain outlets to Nuuanu Stream, Oahu, Hawaii

Outlet[a]	Ir[b]	Pd	Pt	Rh
Judd	0.23 ± 0.036^{d}	5.94 ± 3.67^{c}	10.3 ± 4.66^{c}	0.82 ± 0.68^{c}
	(0.24)	(4.26)	(8.89)	(0.37)
Beretania	0.11 ± 0.017^{c}	10.5 ± 5.23^{d}	15.8 ± 11.0^{cd}	1.38 ± 0.25^{cd}
	(0.11)	(8.33)	(12.3)	(1.35)
Vineyard	0.20 ± 0.042^{d}	12.6 ± 4.52^{d}	24.5 ± 6.74^{e}	2.85 ± 0.78^{d}
	(0.19)	(11.7)	(25.5)	(3.20)

[a] The Judd site is the most upstream of the storm drain outlets sampled and is characterized by residential land use, and has the lowest traffic levels. Both Vineyard and Beretania sites are primarily influenced by commercial land use, and have significantly higher traffic densities

[b] Outlet concentrations for a given element (column-wise) are not significantly different at α = 0.05 if followed by the same letter (c, d, e)

those for the Judd St. outlet. Palladium and Rh were similar between the downstream Vineyard and Beretania storm drain outlets. Platinum was highest in Vineyard sediments. Both Beretania and Vineyard sites are primarily influenced by commercial land uses and have significantly higher traffic densities than the upstream Judd St. outlet. Thus, these three elements show an enrichment that is likely related to the direct delivery of contaminated road sediment to Nuuanu Stream via storm drains.

The autocatalyst-associated Pd, Pt, and Rh exhibited no consistent pattern of higher concentrations at the outlet or immediately downstream (Fig. 2). Although, the PGE values at the Judd outlet (0 m) were generally higher than those upstream (note negative values, i.e., −5, −10, and −20 m, on Fig. 2 reflect upstream sample locations). These patterns suggest that once road runoff, and transported road sediments with their sorbed contaminants, reach the stream via storm drains, they are largely dispersed by unidirectional fluid flows. Thus, the areas in the immediate vicinity of storm drains in Nuuanu Stream do not represent hotspots of contaminant storage.

3.4 *Bivariate Bed Sediment PGE Concentration Associations and Ratio 'Fields'*

Palladium, Pt, and Rh were highly correlated (P-values < 0.0004), with Spearman correlation coefficients (r_S) between 0.79 and 0.87. Highly significant PGE correlations are suggestive of a common source, and we suggest that the most likely source would be release to the environment from automotive catalytic converters. No statistically significant correlation was observed between Ir and the other PGEs (P-values ranged from 0.47 to 0.85). The linear relationships on log-log axes are shown for Pt and Pd (Fig. 3a), Pt and Rh (Fig. 3b), and Pd and Rh (Fig. 3c). Data from 12 RDS samples from the Nuuanu catchment are also shown in Fig. 3a–c.

The close association of bivariate PGE concentration ratios for solid environmental media with those typical of TWCs has been used to infer anthropogenic inputs from autocatalysts (e.g., Whiteley 2005). Three common ratio 'fields' for TWCs have been defined by Ely et al. (2001, p. 3822) based on data published between 1995 and 2000, Pt/Pd 1–2.5, Pt/Rh 5–16, and Pd/Rh 4–9 (superimposed on Fig. 3).

The average (±SD) Pt/Pd ratio for Nuuanu bed sediments (<63 μm) was 1.80 ± 0.46, with a range from 0.62 to 2.59. Nineteen of the 21 bed sediment samples from this study were within the Pt/Pd 'field'. The Nuuanu Pt/Pd ratio was similar to bed sediment data from River Stour, Kent, UK (de Vos et al. 2002) and River Don and tributaries, UK (Prichard et al. 2008). In comparison, the mean Pt/Rh ratio for bed sediments was 12.5 ± 7.0, with a range from 7.0 to 30.0. Sixteen of the 21 bed sediment samples fell within the Pt/Rh 'field'. This ratio is comparable to the average value of 14 from River Stour (de Vos et al. 2002), but higher

Fig. 2 **a** Spatial variation in Pd concentration for bed sediments (<63 μm) associated with three storm drain outlets to Nuuanu Stream. Note *negative values* indicate upstream sample locations. The *horizontal line* represents the average baseline concentration. **b** Pt concentration. **c** Rh concentration, baseline concentration is 0.07 ng g^{-1} (not shown)

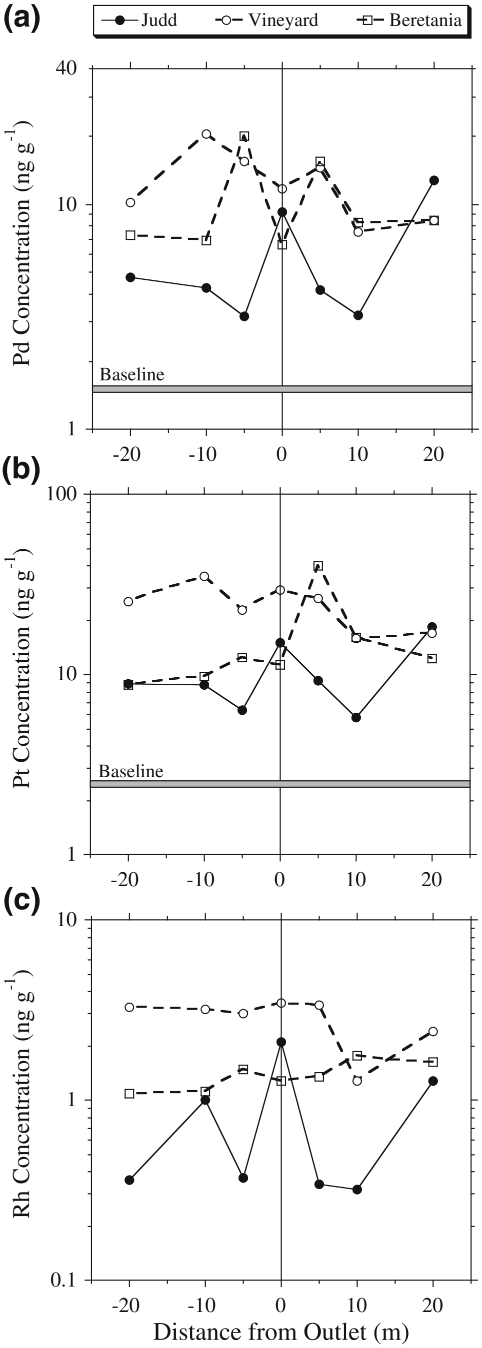
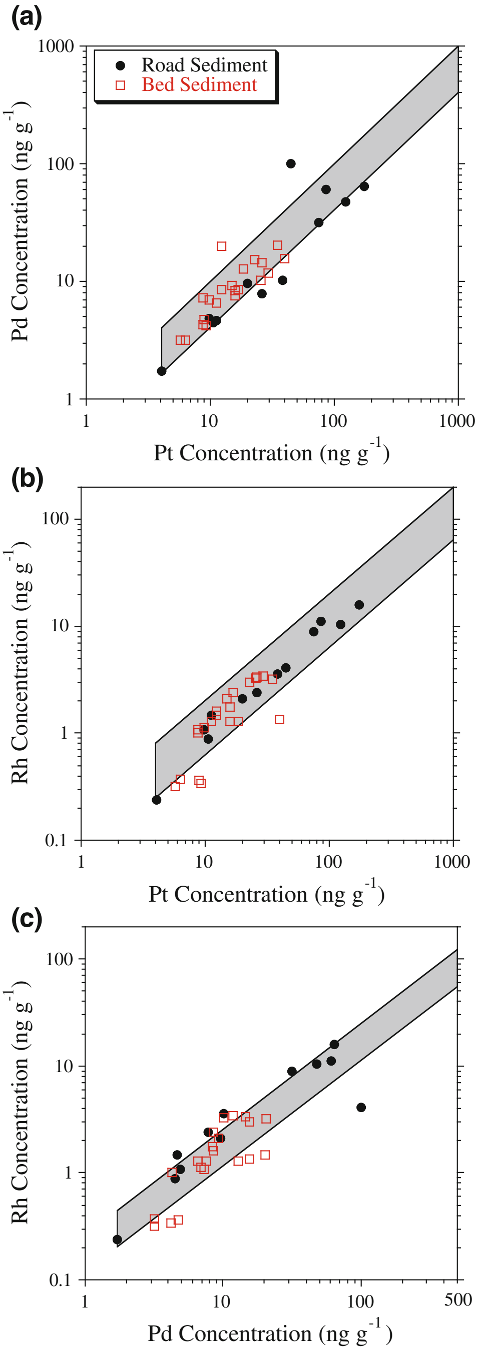


Fig. 3 **a** Bivariate scattergram of Pt and Pd concentrations in bed sediments (<63 μm) from Nuuanu, Stream. The *shaded area* reflects the Pt/Pd ‘field’ of 1–2.5 defined by Ely et al. (2001) for autocatalysts. Data for Nuuanu road deposited sediments are from Sutherland et al. (2008). **b** Pt and Rh concentrations. The *shaded area* reflects the Pt/Rh ‘field’ of 5–16 defined by Ely et al. (2001) for autocatalysts. Data for road sediments are from Sutherland et al. (2008). **c** Pd and Rh concentrations. The *shaded area* reflects the Pd/Rh ‘field’ of 4–9 defined by Ely et al. (2001) for autocatalysts. Data for road sediments are from Sutherland et al. (2008)



than those determined for Shire Brook and River Don, 4.3 and 7.0, respectively (Prichard et al. 2008).

Finally, the average Pd/Rh ratio for this study was 7.0 ± 3.4, with a range from 3.1 to 13.6. The Pd/Rh ratio was the most poorly constrained for Nuuanu, with only 12 of 21 sediment samples falling within the Pd/Rh 'field' defined by Ely et al. (2001). Whiteley and Murray (2005) found only 38 % of their infiltration basin sediments had Pd/Rh ratios that fell within the typical TWC 'field'. They argued that the low inclusion rate was a function of the increased solubility of Pd along the sediment transport path. Furthermore, the Pt/Pd ratio of infiltration basin sediments were statistically greater than those for the contributing RDSs. This was not the case for the Pt/Rh ratios from Nuuanu, which were not statistically different between media. There is evidence in the literature indicating preferential Pd solubility (i.e., Bowles and Gize 2005). Data from the present study indicated no statistically significant difference between RDS and bed sediment Pt/Rh (P-value = 0.38) and Pd/Rh (P-value = 0.57) ratios. However, the Pt/Pd ratio in the source area (i.e., RDS) was significantly greater (P-value = 0.034) than in the sink (bed sediments), 2.3 versus 1.8. These preliminary results do not support preferential loss of Pd along the limited sediment transport pathway from road to river in Nuuanu catchment.

It should be noted that the close approximation of the PGE ratios, especially Pt/Pd and Pt/Rh, in this study to the TWC 'fields' of Ely et al. (2001) reflect the sample collection date of Nuuanu sediments (i.e., 2002). The typical range of values compiled by Ely et al. (2001) do not reflect recent changes in PGE pricing, advances in catalyst washcoat technology, changes in fuel quality, tightening of emission standards, etc. (Cooper and Beecham 2013). The main driver impacting the proportional distribution of PGEs in light-duty gasoline vehicles is pricing. For example, from 2003 through 2010 the cost of Pt significantly exceeded Pd (Fig. 4a) by a factor of 3.1- to 4.5-fold. This price differential can be combined with an order of magnitude increase in the annual pricing of Rh from 2003 ($17.06 US per gram) to 2008 ($210.56 US per gram), and a maximum monthly mean value for Rh of $314.33 US per gram in June of 2008 (Fig. 4b). These price fluctuations have resulted in increased use of Pd at the expense of Pt, and significant thrifting of Rh in TWCs. Today the majority of TWCs are Pd/Rh with Pt much less common (Cooper and Beecham 2013). The temporal variation in PGE proportional loading on TWCs is currently reflected in the PGE ratios observed in solid environmental media (Table 4). It is clear from Table 4 that most cited studies with PGE samples collected after 2004 have ratio 'fields' different from those compiled by Ely et al. (2001). For example: (1) Pt/Pd ratios are more frequently below 1.0, than between 1 and 2.5; (2) Pt/Rh ratios are more frequently below the range of 5–16; and (3) Pd/Rh ratios are equally as likely to fall below or above the typical range of 4–9 compiled by Ely et al. (2001).

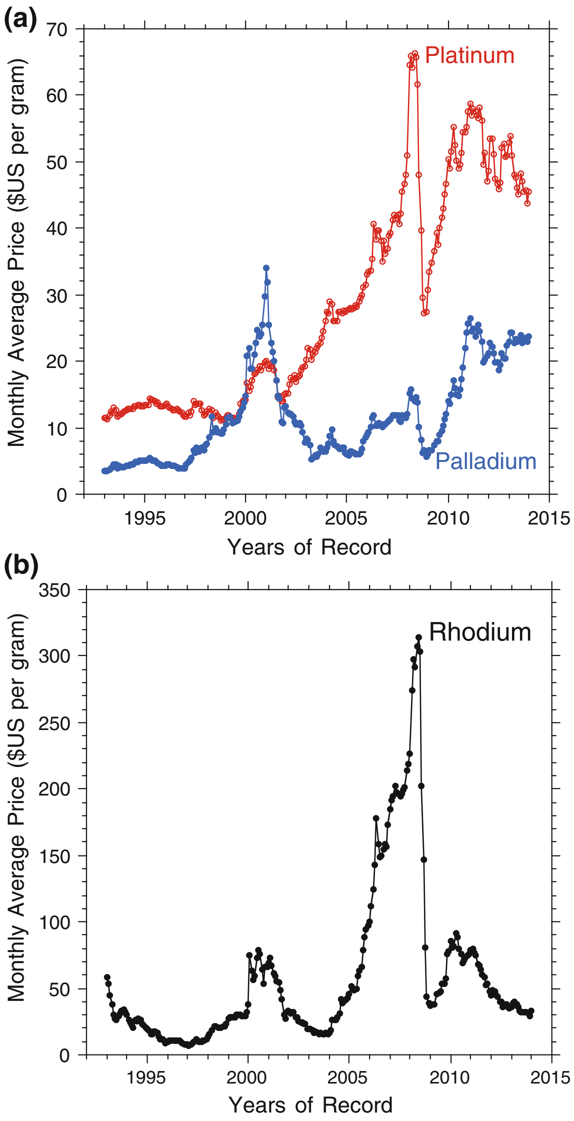


Fig. 4 **a** Monthly variation in Pd and Pt pricing from January 1993 to January 2014. Data accessed January 10, 2014 (www.platinum.matthey.com). **b** Monthly variation in Rh pricing

3.5 Grain Size-Normalized PGE Enrichment Ratios

Median bed sediment ERs (<63 μm) follow the sequence (Table 5): ER_{Rh} (20) > ER_{Pd} (6) = ER_{Pt} (6) > ER_{Ir} (2). Median comparisons between the different solid environmental media indicate anthropogenically impacted ERs for Pd, Pt, and Rh in road sediments exceed those in the stream channel by a factor of 1.2–2.2

Table 4 Summary of selected average PGE ratios for solid environmental media

Location	Media	Date collected	Pt/Pd	Pt/Rh	Pd/Rh	Reference[a]
Europe	Unused autocatalyst	2008	0.68	8.55	12.6	1
Sheffield, U.K.	River sediment (Shire Brook)	2006	0.92	4.33	4.93	2
Sheffield, U.K.	River sediment (Don River)	2006	1.46	7.00	5.00	2
Sheffield, U.K.	Road-deposited sediment	2006	0.92	3.35	4.64	2
Sheffield, U.K.	Estuary sediment	2006	1.10	5.50	5.00	2
Beijing, China	Roadside soil	2007	1.91	3.94	2.06	3
Guangzhou, China	Roadside soil	2007	0.88	2.90	3.30	3
Hong Kong, China	Roadside soil	2007	1.61	5.76	3.58	3
Macao, China	Roadside soil	2007	0.88	4.21	4.80	3
Qingdao, China	Roadside soil	2007	1.00	3.24	3.25	3
Kolkata, India	Roadside soil	2007	1.98	5.43	2.75	3
Mumbai, India	Roadside soil	2007	0.40	9.75	24.2	3
Varese, Italy	Leaf-deposited dust	2004–2005	0.86	1.59	1.84	4
Varese, Italy	Leaf-deposited dust	2007	0.29	0.54	1.85	4
Sheffield, U.K.	Sewage sludge	2004–2006	0.98	23.0	20.0	5
			(0.45–1.51)[b]	(9.00–40.0)	(16.5–26.5)	
Sheffield, U.K.	Incinerator ash (raw)	2004–2006	0.94	7.44	9.55	5
			(0.66–1.30)[b]	(3.40–16.8)	(3.44–17.7)	
Birmingham, U.K.	Sewage sludge	2004–2006	1.41	29.3	18.8	5
			(0.77–1.70)[b]	(8.71–32.0)	(11.2–20.8)	

(continued)

Table 4 (continued)

Location	Media	Date collected	Pt/Pd	Pt/Rh	Pd/Rh	Reference[a]
Birmingham, U.K.	Incinerator ash (raw)	2004–2006	0.91	14.1	15.1	5
			(0.80–1.13)[b]	(11.4–21.5)	(11.9–19.8)	
Modena, Italy	Nature reserve soil	2004	0.60	2.40	4.00	6
Modena, Italy	Agricultural soil	2004	0.68	2.87	4.20	6
Modena, Italy	Suburban soil	2004	0.65	5.20	7.94	6
Modena, Italy	Urban soil	2004	0.76	6.53	8.59	6
Hyderabad, India	Road-deposited sediment	2007	0.80	6.83	9.28	7
			(0.14–7.50)[b]	(2.00–16.0)	(2.00–30.0)	
Beijing, China	Road-deposited sediment	2010	0.49	2.88	5.87	8
U.S.A.	Spent autocatalyst	2011	0.71	4.42	6.24	9
Texas, U.S.	Washburn Tunnel dust	2013	0.70	3.2–4.4	5.2	9
Houston, TX, U.S.	Road-deposited sediment	2013	1.5–3.5	11.5–20.9	3.9–14.1	9
Guangzhou, China	Road-deposited sediment	2009	0.87	3.33	3.84	10
Texas, U.S.	Washburn Tunnel $PM_{2.5}$	2012–2013	0.31	2.3	7.6	11
Texas, U.S.	Washburn Tunnel PM_{10}	2012–2013	0.24	1.4	5.9	11
Europe	Various	1995–2000	1.0–2.5	5–16	4–9	12
This study	Fluvial bed sediment	2002	1.84	8.73	5.53	
			(0.62–2.59)[b]	(7.03–30.0)	(3.11–13.6)	

[a] 1. LGC Limited (2008), ERM-EB503a; 2. Prichard et al. (2008); 3. Pan et al. (2009); 4. Fumagalli et al. (2010); 5. Jackson et al. (2010); 6. Marcheselli et al. (2010); 7. Mathur et al. (2011); 8. Gao et al. (2012); 9. Spada et al. (2012); 10. Zhong et al. (2012); 11. Bozlaker et al. (2014); 12. Ely et al. (2001)

[b] Median values with minimum and maximum values in parentheses

Table 5 Mean ± SD (median in parentheses) enrichment ratios for PGEs in bed sediment (BS) and road-deposited sediment (RDS) in Nuuanu watershed, Oahu, Hawaii

Element	Bed sediment (n = 21)	Road-deposited sediment[a] (n = 12)	Median $\frac{\text{RDS}}{\text{BS}}$
Ir	2.3 ± 0.8	2.8 ± 4.2	0.74
	(2.3)	(1.7)	
Pd	6.9 ± 3.7	20.9 ± 23.3	1.2
	(6.1)	(7.1)	
Pt	6.8 ± 3.9	20.8 ± 21.3	2.1
	(6.0)	(12.9)	
Rh	25.3 ± 15.8	77.7 ± 76.4	2.2
	(20.2)	(44.6)	

[a] Computed using data compiled during the Sutherland et al. (2008) study

(Table 5). Iridium displayed a geogenic signal, having a higher median ER in bed sediments than in road sediments (ratio = 0.7).

When median ERs were computed using data reported by Ely et al. (2001) for 13 roadside soils and background soil data from Indiana, a sequence similar to Nuuanu was found: ER_{Rh} (15) > ER_{Pt} = ER_{Pd} (4). Similarly, ERs for 12 infiltration basin sediments and one wetland sediment in Perth, Australia were computed using the background soil data reported by Whiteley and Murray (2005). The median ER sequence was: ER_{Pt} (55) > ER_{Rh} (30) > ER_{Pd} (15). Enrichment data from the Nuuanu study, combined with those from the literature provide evidence of a strong anthropogenic signal for Pd, Pt, and Rh.

Rhodium may therefore be one of the most useful elements to fingerprint vehicle-associated sediment inputs to catchments over the last 20–30 years. For example, its limited post-depositional environmental mobility compared to Pd is an asset. Rhodium typically has significantly lower background concentrations in soil and bedrock compared with Pt. In the present study, average background concentrations of Pd and Pt exceed Rh by 21- and 37-fold, respectively. Despite the higher inputs of Pt from autocatalysts to the environment, ER_{Rh}-values are typically as high or higher than Pt. This has recently been documented for Washburn Tunnel (Houston, Texas) dust samples, and for $PM_{2.5}$ and PM_{10} samples collected in the same tunnel (Spada et al. 2012; Bozlaker et al. 2014). Further support for Rh as an indicative element for anthropogenic contamination comes from the fact that Pt is a common element in antitumour agents (cisplatin and carboplatin) and is highly concentrated in the waste stream of medical facilities (Ravindra et al. 2004). Inadvertent release of Pt to the fluvial environment prior to treatment, or even after treatment to coastal ecosystems, would complicate the interpretation of the Pt fingerprint signal in sedimentary sinks.

3.6 *Grain-Size Fractionated Storm-Drain Associated Bed Sediment Sample*

The limited attention paid to the variation of PGEs in different sediment or soil grain size fractions in the environmental literature may be based on the general assumption that element concentration typically increases with decreasing grain size, because of greater surface area and greater sorption potential (*cf.* Horowitz 1991). In contrast to this notion, Sutherland et al. (2008) found significantly higher concentrations of autocatalyst PGEs in fractions >63 µm for road sediments. Data for the fractionated Vineyard storm drain outlet sample examined in this study also exhibited higher concentrations of autocatalyst PGEs in fractions coarser than 63 µm (Table 6). Considering analytical error, concentrations of Ir were similar in all grain size fractions examined. The maximum concentration for Pd was in the coarse sand-sized fraction (500–1,000 µm) at 35 ng g^{-1}. The maximum concentration for Pt was in the fine sand-sized fraction (125–250 µm), containing 63 ng g^{-1}; and the maximum concentration of 6.8 ng g^{-1} for Rh was found in the very fine-sized sand fraction (63–125 µm). The ratio of the grain-size fraction with the maximum concentration to the concentration in the <63 µm fraction were 1.0 (Ir), 2.0 (Rh), 2.1 (Pt), and 3.0 (Pd) (Table 6).

Median enrichment values for the five Vineyard sediment fractions >63 µm (minimum and maximum values in parentheses) followed the order: $ER_{Rh} = 47$ (6–102) > $ER_{Pd} = 16$ (1–25) = $ER_{Pt} = 14$ (1–21) ≫ $ER_{Ir} = 1.5$ (1.4–1.6). Except for the coarsest fraction analyzed (1–2 mm), the autocatalyst PGEs exhibited significant anthropogenic enrichment in bed sediments of Nuuanu Stream.

Maximum mass loading (GSF_{Load}) for Pd and Pt were observed in the coarse sand-sized fraction (500–1,000 µm) at 60 % and 32 %, respectively (Fig. 5).

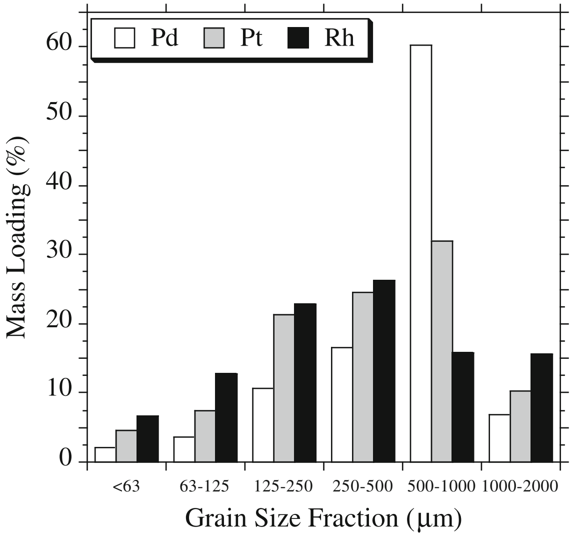
Table 6 Grain size distribution and PGE concentrations (ng g^{-1}) in specific size fractions isolated by sieving of the Vineyard storm drain outlet bed sediment sample, Nuuanu Stream, Oahu, Hawaii

Grain size (µm)	Sedimentological description	Mass (%)	Ir[a]	Pd	Pt	Rh
<63	Silt and clay	2.5	**0.17**	11.7	29.4	3.46
63–125	Very fine sand	2.4	0.12	22.2	48.6	**6.79**
125–250	Fine sand	5.4	*0.11*	29.1	**62.6**	5.46
250–500	Medium sand	11.0	0.13	22.2	35.3	3.10
500–1,000	Coarse sand	25.6	0.13	**34.6**	19.8	0.80
1,000–2,000	Very coarse sand	53.1	0.12	*1.9*	*3.0*	*0.38*
$\frac{\text{Max}^{b}}{<63}$	–		1	3.0	2.1	2.0

[a] For a given PGE, *italic* values reflect the minimum concentration observed, and those that are in **bold** reflect the maximum concentration

[b] For a given PGE, this index represents the ratio of the maximum element concentration to that for the <63 µm grain size fraction

Fig. 5 Mass loading percentages of Pd, Pt, and Rh in the grain-size fractionated Vineyard storm drain outlet sediment sample



For Rh, the maximum GSF_{Load} was in the medium sand-sized fraction (250–500 μm) at 26 %. Mass loading data indicate further attention must be given to quantifying PGEs in a variety of grain sizes, and not only in the most commonly analyzed fraction, e.g., <63 μm.

Jarvis et al. (2001) reported higher concentrations of PGEs in coarser fractions of road sediments above certain concentration thresholds. They speculated that agglomeration had occurred. This may partially account for the highest concentrations of PGEs in fractions >63 μm, as these elements have typical diameters of 1–10 nm when fixed on the surface of the washcoat of the monolithic honeycomb catalytic converters (Ravindra et al. 2004). Sintering and erosion of TWCs, with subsequent emission of PGEs in association with converter washcoat particles of γ–Al_2O_3 (Rauch and Morrison 2008) may also account for some of the PGEs in coarser fractions. However, we are not aware of any research that has shown emitted washcoat particles with associated PGEs coarser than 500 μm. Another possible reason for high concentrations of PGEs in coarse fractions is the charge characteristics of the organo-clay complexes in aggregated sediments in Nuuanu catchment. High cation exchange capacity (CEC) was observed for 11 bulk (<2 mm) sediment samples from Nuuanu Stream (Sutherland unpublished data). Mean CECs were 38.2 ± 3.9 meq 100 g^{-1}, with a range from 27.7 to 42.6 meq 100 g^{-1}. Additional grain size fractionated CEC data are not available to further test this hypothesis.

4 Conclusions

This is the first published study that combines both a detailed spatial examination of PGE abundance and grain size partitioning in fluvial bed sediments of an urban river. Data support strong anthropogenic contamination signals for Pd, Pt, and Rh in all bed sediment grain size fractions <1 mm. Rhodium was the element that was most enriched in Nuuanu streambed sediments, followed by Pd and Pt. The enrichment of PGEs in Nuuanu Stream is interpreted to be first from attrition of TWCs and subsequent emission via automotive exhaust and deposition on the road environment. Secondly, road runoff transfers the particle-associated anthropogenic PGEs via storm drains directly to the fluvial network.

Preliminary grain size partitioning data indicate that further attention should be given to examining PGEs in a variety of size fractions of solid environmental media. The finest grain-size fraction sampled for bed sediment in Nuuanu Stream (<63 μm) had the lowest autocatalyst-associated PGE concentrations and the lowest mass loading percentages. Further data are required to confirm the relationship of PGEs and grain size. Additionally, further examination of processes responsible for preferential association of PGEs with coarser grain size fractions is necessary. Accurate quantification of enrichment ratios can only be made with full knowledge of the grain size partitioning of the system under study. Finally, the use of Rh as an element for identifying urban sediment inputs in catchment sediment source and sediment budgeting studies should be further explored.

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References

Acres GJK, Harrison B (2004) The development of catalysts for emission control from motor vehicles: early research at Johnson Matthey. Top Catal 28:3–11

Akrivi AA, Tsogas GZ, Gioikas DL, Vlessidis AG (2012) Analytical determination and biomonitoring of platinum group elements in roadside grass using microwave assisted digestion and electrothermal atomic absorption spectrometry. Anal Lett 45:526–538

Aleksander-Kwaterczak U, Helios-Rybicka E (2009) Contaminated sediments as a potential source of Zn, Pb, and Cd for a river system in the historical metalliferous ore mining and smelting industry area of south Poland. J Soil Sediment 9:13–22

Andrews S, Sutherland RA (2004) Cu, Pb, Zn contamination in Nuuanu watershed, Oahu, Hawaii. Sci Total Environ 324:173–182

Bennett VC, Norman MD, Garcia MO (2000) Rhenium and platinum group element abundances correlated with mantle source components in Hawaiian picrites: sulphides in the plume. Earth Planet Sci Lett 183:513–526

Bowles JFW, Gize AP (2005) A preliminary study of the release of platinum and palladium from metallic particles in the surface environment by organic acids: relevance to weathering of particles from vehicle exhaust catalysts. Mineral Mag 69:687–693

Bozlaker A, Spada NJ, Fraser MP, Chellam S (2014) Elemental characterization of $PM_{2.5}$ and PM_{10} emitted from light duty vehicles in the Washburn Tunnel of Houston, Texas: release of rhodium, palladium, and platinum. Environ Sci Technol 48:54–62

Brasher AM, Anthony SS (2000) Occurrence of organochlorine pesticides in stream bed sediments and fish from selected streams on the island of Oahu, Hawaii, 1998. U.S. Geological Survey Fact Sheet 140-00, U.S. Government Printing Office, Washington

Colombo C, Monhemius AJ, Plant JA (2008a) Platinum, palladium and rhodium release from vehicle exhaust catalysts and road dust exposed to simulated lung fluids. Ecotoxicol Environ Saf 71:722–730

Colombo C, Monhemius AJ, Plant JA (2008b) The estimation of the bioavailabilities of platinum, palladium and rhodium in vehicle exhaust catalysts and road dusts using a physiologically based extraction test. Sci Total Environ 389:46–51

Cooper J, Beecham J (2013) A study of platinum group metals in three-way autocatalysts. Platin Met Rev 57:281–288

Crocket JH (2000) PGE in fresh basalt, hydrothermal alteration products, and volcanic incrustations of Kilauea Volcano, Hawaii. Geochim Cosmochim Acta 64:1791–1807

de Vos E, Edwards SJ, McDonald I, Wray DS, Carey PJ (2002) A baseline survey of the distribution and origin of platinum group elements in contemporary fluvial sediments of the Kentish Stour, England. Appl Geochem 17:1115–1121

Djingova R, Kovacheva P, Wagner G, Markert B (2003) Distribution of platinum group elements and other traffic related elements among different plants along some highways in Germany. Sci Total Environ 308:235–246

Ek KH, Morrison GM, Rauch S (2004) Environmental routes for platinum group elements to biological materials—a review. Sci Total Environ 334–335:21–38

Ely JC, Neal CR, Kulpa CF, Schneegurt MA, Seidler JA, Jain JC (2001) Implications of platinum-group element accumulation along U.S. roads from catalytic-converter attrition. Environ Sci Technol 35:3816–3822

Fliegel D, Berner Z, Eckhardt D, Stüben D (2004) New data on the mobility of Pt emitted from catalytic converters. Anal Bioanal Chem 379:131–136

Fumagalli A, Faggion B, Ronchini M, Terzaghi G, Lanfranchi M, Chirico N, Cherchi L (2010) Platinum, palladium, and rhodium deposition to the *Prunus laurus cerasus* leaf surface as an indicator of the vehicular traffic pollution in the city of Varese area. Environ Sci Pollut Res 17:665–673

Gao B, Yu Y, Zhou H, Lu J (2012) Accumulation and distribution characteristics of platinum group elements in roadside dusts in Beijing, China. Environ Toxicol Chem 31:1231–1238

Gao B, Zhou H, Huang Y, Wang Y, Gao J, Liu X (2014) Characteristics of heavy metals and Pb isotopic composition in sediments collected from the tributaries in Three Gorges Reservoir, China. Sci World J. http://dx.doi.org/10.1155/2014/685834

Horowitz AJ (1991) A primer on sediment-trace element chemistry. CRC Press, Boca Raton

Hutchinson EJ, Pearson PJG (2004) An evaluation of the environmental and health effects of vehicle exhaust catalysts in the United Kingdom. Environ Health Perspect 112:132–141

Jackson MT, Sampson J, Prichard HM (2007) Platinum and palladium variations through the urban environment: evidence from 11 sample types from Sheffield, UK. Sci Total Environ 385:117–131

Jackson MT, Prichard HM, Sampson J (2010) Platinum-group elements in sewage sludge and incinerator ash in the United Kingdom: assessment of PGE sources and mobility in cities. Sci Total Environ 408:1276–1285

Jamais M, Lassiter JC, Brugmann G (2008) PGE and Os-isotopic variations in lavas from Kohala Volcano, Hawaii: constraints on PGE behavior and melt/crust interaction. Chem Geol 250:16–28

Jarvis KE, Parry SJ, Piper JM (2001) Temporal and spatial studies of autocatalyst-derived platinum, rhodium, and palladium and selected vehicle-derived trace elements in the environment. Environ Sci Technol 35:1031–1036

Kalavrouziotis IK, Koukoulakis PH (2009) The environmental impact of the platinum group elements (Pt, Pd, Rh) emitted by the automobile catalyst converters. Water Air Soil Poll 196:393–402

Kanitsar K, Koellensperger G, Hann S, Limbeck A, Puxbaum H, Stingeder G (2003) Determination of Pt, Pd and Rh by inductively coupled plasma sector field mass spectrometry (ICP-SFMS) in size-classified urban aerosol samples. J Anal At Spectrom 18:239–246

Kaspar J, Fornasiero P, Hickey N (2003) Automotive catalytic converters: current status and some perspectives. Catal Today 77:419–449

Lee H-Y, Chon H-T, Sager M, Marton L (2012) Platinum pollution in road dusts, roadside soils, and tree barks in Seoul, Korea. Environ Geochem Health 34:5–12

Limited LGC (2008) Certificate of analysis: ERM-EB503a (Platinum group elements in unused automobile catalyst). Middlesex, London

Lucena P, Vadillo JM, Laserna JJ (1999) Mapping of platinum group metals in automotive exhaust three-way catalysts using laser-induced breakdown spectrometry. Anal Chem 71:4385–4391

Marcheselli M, Sala L, Mauri M (2010) Bioaccumulation of PGEs and other traffic-related metals in populations of the small mammal *Apodemus sylvaticus*. Chemosphere 80:1247–1254

Mathur R, Balaram V, Satyanarayanan M, Sawant SS, Ramesh SL (2011) Anthropogenic platinum, palladium and rhodium concentrations in road dusts from Hyderabad City, India. Environ Earth Sci 62:1085–1098

Meisel T, Moser J (2004) Platinum-group element and rhenium concentrations in low abundance reference materials. Geostand Geoanal Res 28:233–250

Meisel T, Fellner N, Moser J (2003) A simple procedure for the determination of platinum group elements and rhenium (Ru, Rh, Pd, Re, Os, Ir and Pt) using ID-ICP-MS with an inexpensive on-line matrix separation in geological and environmental materials. J Anal At Spectrom 18:720–726

Milacic R, Scancar J, Murko S, Kocman D, Horvat M (2010) A complex investigation of the extent of pollution in sediments of the Sava River. Part 1: Selected elements. Environ Monit Assess 163:263–275

Morton O, Puchelt H, Hernández E, Lounejeva E (2001) Traffic-related platinum group elements (PGE) in soils from Mexico City. J Geochem Explor 72:223–227

Nischkauer W, Herincs E, Puschenreiter M, Wenzel W, Limbeck A (2013) Determination of Pt, Pd and Rh in *Brassica napus* using solid sampling electrothermal vaporization inductively coupled plasma optical emission spectrometry. Spectrochim Acta B 89:60–65

Norman MD, Garcia MO, Bennett VC (2004) Rhenium and chalcophile elements in basaltic glasses from Koolau and Molokai Volcanoes: magmatic outgassing and composition of the Hawaiian plume. Geochim Cosmochim Acta 68:3761–3777

Owens PN, Caley KA, Campbell S, Koiter AJ, Droppo IG, Taylor KG (2011) Total and size-fractionated mass of road-deposited sediment in the city of Prince George, British Columbia, Canada: implications for air and water quality in an urban environment. J Soil Sediment 11:1040–1051

Palacios MA, Gómez MM, Moldovan M, Morrison GM, Rauch S, McLeod C, Ma R, Laserna J, Lucena P, Caroli S, Alimonti A, Petrucci F, Bocca B, Schramel P, Lustig S, Zischka M, Wass U, Stenbom B, Luna M, Saenz JC, Santamaría J, Torrens JM (2000) Platinum-group elements: quantification in collected exhaust fumes and studies of catalysts surfaces. Sci Total Environ 257:1–15

Pan S, Zhang G, Sun Y, Chakraborty P (2009) Accumulating characteristics of platinum group elements (PGE) in urban environments, China. Sci Total Environ 407:4248–4252

Park J-W, Hu Z, Gao S, Campbell IH, Gong J (2012) Platinum group element abundances in the upper continental crust revisited—new constraints from analyses of Chinese loess. Geochim Cosmochim Acta 93:63–76

Peucker-Ehrenbrink B, Bach W, Hart SR, Blusztajn JS, Abbruzzese T (2003) Rhenium-osmium isotope systematics and platinum group element concentrations in oceanic crust from DSDP/ODP sites 504 and 417/418. Geochem Geophys Geosyst. doi:10.1029/2002GC000414

Pitcher L, Helz RT, Walker RJ, Piccoli P (2009) Fractionation of the platinum-group elements and Re during crystallization of basalt in Kilauea Iki Lava Lake, Hawaii. Chem Geol 260:196–210

Pratt C, Lottermoser BG (2007) Mobilisation of traffic-derived trace metals from road corridors into coastal stream and estuarine sediments, Cairns, northern Australia. Environ Geol 52:437–448

Prichard HM, Fisher PC (2012) Identification of platinum and palladium particles emitted from vehicles and dispersed into the surface environment. Environ Sci Technol 46:3149–3154

Prichard HM, Jackson MT, Sampson JJ (2008) Dispersal and accumulation of Pt, Pd and Rh derived from a roundabout in Sheffield (UK): from stream to tidal estuary. Sci Total Environ 401:90–99

Puls C, Limbeck A, Hann S (2012) Bioaccessibility of palladium and platinum in urban aerosol particulates. Atmos Environ 55:213–219

Radakovitch O, Roussiez V, Ollivier P, Ludwig W, Grenz C, Probst J-L (2008) Input of particulate heavy metals from rivers and associated sedimentary deposits on the Gulf of Lion continental shelf. Estuar Coast Shelf Sci 77:285–295

Rauch S, Morrison GM (2008) Environmental relevance of the platinum-group elements. Elements 4:259–263

Rauch S, Hemond HF, Peucker-Ehrenbrink B (2004) Recent changes in platinum group element concentrations and osmium isotopic composition in sediments from an urban lake. Environ Sci Technol 38:396–402

Ravindra K, Bencs L, Van Grieken R (2004) Platinum group elements in the environment and their health risk. Sci Total Environ 318:1–43

Riga-Karandinos AN, Saitanis C (2004) Biomonitoring of concentrations of platinum group elements and their correlations to other metals. Int J Environ Pollut 22:563–579

Saeedi M, Li LY, Karbassi AR, Zanjani AJ (2013) Sorbed metals fractionation and risk assessment of release in river sediment and particulate matter. Enivon Monit Assess 185:1737–1754

Spada N, Bozlaker A, Chellam S (2012) Multi-elemental characterization of tunnel and road dusts in Houston, Texas using dynamic reaction cell-quadrupole-inductively coupled plasma-mass spectrometry: evidence for the release of platinum group and anthropogenic metals from motor vehicles. Anal Chim Acta 735:1–8

Sutherland RA (2003) Lead in grain size fractions of road-deposited sediment. Environ Pollut 121:229–237

Sutherland RA (2007) A re-examination of platinum-group element concentrations in the environmental certified reference material BCR-723. Int J Environ Anal Chem 87:501–520

Sutherland RA, Pearson DG, Ottley CJ (2007) Platinum-group elements (Ir, Pd, Pt and Rh) in road-deposited sediments in two urban watersheds, Hawaii. Appl Geochem 22:1485–1501

Sutherland RA, Pearson DG, Ottley CJ (2008) Grain size partitioning of platinum-group elements in road-deposited sediments: implications for anthropogenic flux estimates from autocatalysts. Environ Pollut 151:503–515

Tatsumi Y, Oguri K, Shimoda G (1999) The behaviour of platinum-group elements during magmatic differentiation in Hawaiian tholeiites. Geochem J 33:237–247

Tuit CB, Ravizza GE, Bothner MH (2000) Anthropogenic platinum and palladium in the sediments of Boston Harbor. Environ Sci Technol 34:927–932

Wedepohl KH (1995) The composition of the continental crust. Geochim Cosmochim Acta 59:1217–1232

Wei C, Morrison GM (1994a) Platinum analysis and speciation in urban gullypots. Anal Chim Acta 284:587–592

Wei C, Morrison GM (1994b) Platinum in road dusts and urban river sediments. Sci Total Environ 146(147):169–174

Whiteley JD (2005) Seasonal variability of platinum, palladium and rhodium (PGE) levels in road dusts and roadside soils, Perth, Western Australia. Water Air Soil Pollut 160:77–93

Whiteley JD, Murray F (2003) Anthropogenic platinum group element (Pt, Pd and Rh) concentrations in road dusts and roadside soils from Perth, Western Australia. Sci Total Environ 317:121–135

Whiteley JD, Murray F (2005) Autocatalyst-derived platinum, palladium and rhodium (PGE) in infiltration basin and wetland sediments receiving urban runoff. Sci Total Environ 341:199–209

Wiseman CLS, Zereini F (2009) Airborne particulate matter, platinum group elements and human health: a review of recent evidence. Sci Total Environ 407:2493–2500

Wren M, Gagnon ZE (2014) A histopathological study of Hudson River crayfish, *Orconectes virilis*, exposed to platinum group metals. J Environ Sci Health A 49:135–145

Zar JH (1996) Biostatistical analysis, 3rd edn. Prentice-Hall, Upper Saddle River

Zereini F, Wiseman C, Beyer JM, Artelt S, Urban H (2001) Platinum, lead and cerium concentrations of street particulate matter (Frankfurt am Main, Germany). J Soil Sediment 1:188–195

Zhong L, Li J, Yan W, Tu X, Huang W, Zhang X (2012) Platinum-group and other traffic-related heavy metal contamination in road sediment, Guangzhou, China. J Soil Sediment 12:942–951

Zimmermann S, Messerschmidt J, von Bohlen A, Sures B (2005) Uptake and bioaccumulation of platinum group metals (Pd, Pt, Rh) from automobile catalytic converter materials by the zebra mussel (*Dreissena polymorpha*). Environ Res 98:203–209

Zischka M, Schramel P, Muntau H, Rehnert A, Gómez MG, Wannemaker G, Dams R, Quevauviller P, Maier EA (2002a) The certification of the contents (mass fractions) of palladium, platinum and rhodium in road dust, BCR-723. Institute for Reference Materials and Measurements European Commission BCR Certificate Information, EUR 20307 EN, Geel

Zischka M, Schramel P, Muntau H, Rehnert A, Gómez MG, Stojanik B, Wannemaker G, Dams R, Quevauviller P, Maier EA (2002b) A new certified reference material for the quality control of palladium, platinum and rhodium in road dust, BCR-723. Trend Anal Chem 21:851–868

Long-Term Monitoring of Palladium and Platinum Contents in Road Dust of the City of Munich, Germany

Holger Sievers and Michael Schuster

Abstract The concentration of platinum group metals (PGM), namely palladium, platinum and rhodium, has increased in all earth spheres, which is mainly due to the worldwide use of automotive catalytic converters containing these metals as active components. Especially high concentrations are therefore found near busy roads and in urban environments where PGM concentrations now have reached a level that has let scientists and engineers think about possibilities to recycle these precious metals in the context of urban mining strategies. Especially palladium has been classified as particularly critical as it shows a comparatively high mobility in environmental compartments and elevated toxicological effects. It is therefore advisable and necessary to monitor traffic related PGM emissions with particular focus on palladium. One way to do this is long-term monitoring of PGM emissions under largely constant conditions. In the present work this has been done by monitoring palladium concentrations in tunnel dust of the outer city ring (B2R) of Munich, Germany. Dust samples were collected from 1994 until 2012 from the roofs of emergency telephone boxes installed in the tunnels Landshuter Allee, Candid and Trappentreu and analyzed for their palladium and some of them for their platinum content. Major and minor matrix components have also been analyzed to ensure comparability of the samples. PGM Analysis was performed with Graphite Furnace Atomic Absorption Spectrometry (GFAAS) after complete sample digestion and enrichment of palladium and platinum with N,N-Dialkyl-N' -benzoylthioureas acting as highly selective chelating agents. Matrix characterization was performed by elementary analysis and Total Reflection X-ray Fluorescence (TXRF). The main matrix components determined in the road dust samples from 1994 to 2012 show, apart from one noteworthy exception (sulfur) a quite constant composition. The sulfur content in the dust samples of all three tunnels decreased significantly in the years after 1998. This is most probably attributable to the legally

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required reduction of the sulphur content in gasoline and diesel fuels. The average palladium concentration in the dust samples increased significantly from 1994 to 2007 where it reached a maximum. From 2009 onwards there was a steady decline in the average palladium concentration, reaching a minimum in 2012. The increase of the palladium concentration in the tunnel dust from 1994 to 2007 can easily be explained by the gradual replacement of platinum by palladium in automotive catalytic converters. In 2007 traffic density monitored by the municipal administration of the city of Munich also reached a high level which roughly remained the same up to today. Platinum concentration in the dust samples also reached a maximum in 2007 and declined from 2007 to 2012. The most likely explanation for the decline of the palladium and platinum concentration in the tunnel dust after 2007 is progress in the production of automotive catalytic converters and/or progress in automobile engine construction.

1 Introduction

In Europe car exhaust catalysts are legally prescribed for now 27 years, first in Switzerland (1986), later in Austria and Sweden and since 1993 they are a legal obligation for all newly registered petrol-engined cars in the European Union. Tax incentives first in Germany (1984) and later in other European countries further accelerated the use and the continued development of this technology until today. In parts of the United States of America which have advanced further in car exhaust cleaning technology catalysts have been legally prescribed as early as 1974.

As an inevitable consequence, the concentration of platinum group metals (PGM), namely palladium, platinum and rhodium, which are the catalytically active components in modern car exhaust catalysts, has increased significantly in all earth spheres, i.e. hydrosphere, atmosphere, lithosphere and biosphere. Even in Greenland ice samples an increase in PGM concentration has been detected (Barbante et al. 2001). This is due to the unavoidable discharge of PGM containing particulate matter mobilized by vibrations and material stresses mainly caused by the fast streaming exhaust gases leaving car engines after fuel combustion. Especially high concentrations are found near busy roads (Rauch et al. 2005; Whiteley and Murry 2005; Zereini et al. 2007; Jackson et al. 2007) and in other urban environments where PGM concentrations have reached a level that has let scientists and engineers think about possibilities to recycle these precious metals e.g. from road dust or solid residues of the street drainage system. It is conceivable that in the nearer future PGM recycling from traffic related emissions will be a part of urban mining strategies.

Among other PGM used in car exhaust catalysts palladium has been classified as particularly critical as it shows a comparatively high mobility in environmental compartments and elevated toxicological effects (Aberer et al. 1993; Schäfer et al. 1998; Kristine et al. 2004; Vamnes et al. 2004). It is therefore advisable and necessary to monitor traffic related PGM emissions with particular focus on palladium.

One way to do this is long-term monitoring of PGM emissions under largely constant conditions. In the present work this has been done by monitoring palladium concentrations in tunnel dust of the outer city ring (B2R) of Munich, Germany (Leopold et al. 2008). Dust samples were collected from 1994 until 2012 from the roofs of emergency telephone boxes installed in the tunnels Landshuter Allee, Candid and Trappentreu and analyzed for their palladium and most of them for their platinum content. Major and minor matrix components have also been analyzed to ensure comparability of the samples. These locations have been chosen for some reasons: (1) Weather related influences are reduced to a minimum. (2) Traffic is monitored by the municipal administration and the data are updated regularly. (3) The speed of vehicles in the tunnels is limited to 60 km h^{-1} and is subject to frequent inspection in order to achieve a regular and constant traffic flow (and a greater safety in the tunnels). (4) Only small dust particles settle on the roofs, course particles and litter do not.

2 Special Aspects in Trace and Ultra-Trace Analysis of Palladium

Quantification of palladium in the μg kg^{-1} and ng kg^{-1} range is not straight forward, especially in samples such as road dust, soil or sewing sludge ash, which represent a complex matrix consisting of a large number of elements and element species at concentrations usually exceeding that of palladium by several orders of magnitude. This is aggravated by the fact that some of the most sensitive determination techniques such as Neutron Activation Analysis (NAA) and ICP-MS suffer from severe interference by ubiquitous elements. From an analytical point of view it is therefore advisable to apply selective enrichment procedures, which eliminate matrix influences and, as an additional option, improve the detection limit to make palladium analysis accessible to determination techniques less sensitive but also less susceptible for interferences, e.g. Graphite Furnace Atomic Absorption Spectrometry (GFAAS) or Total Reflection X-ray Fluorescence (TXRF).

One of the oldest, but still very effective procedures to do so are fire assay techniques which do not require dissolution of the samples by aggressive solvents and as a consequence of the method inherent high sample weight, have less problems with statistically unequal distribution of the analyte within the matrix. This is a frequently underestimated problem in modern trace analysis usually performed with low sample weights of several milligrams up to 500 mg. However, before this advantage of fire assay techniques can be exploited to the full, large sample quantities of at least 100 g or more should be available. Fire assays also require special equipment and considerable experience and knowledge especially in finding the appropriate sample adapted mixture of chemicals, optimized temperature profiles and optimal dissolution conditions for the collector phase to avoid loss of analyte (Zereini et al. 1993, 1994, 2007).

Most of the established enrichment procedures require dissolution of the samples, e.g. by high pressure acid digestion, nowadays mostly performed with microwave assistance as a fast energy transmission and heating procedure. In this context it is of outmost importance to achieve a complete dissolution of the samples. The simple and very popular method of determining only the *aqua regia* soluble fraction of elements is very risky, especially in the case of silicate residues which due to their large amorphous surface pose a high risk to bind palladium species in the ng L^{-1} range. Own studies and experiments have demonstrated that between 5 and 90 % of palladium traces can be irreversibly and in a non-reproducible manner bound by silicate residues after *aqua regia* digestion of samples with high silicon content, e.g. road dust and grass samples. In practice, this means that hydrofluoric acid is crucial to completely dissolve silicon containing samples. In most cases the surplus of hydrofluoric acid has to be removed before measurement, e.g. by evaporating it in specially equipped exhaust hoods. This is a very unpopular approach and in addition to the always existing possibility of adsorbing palladium on vessel walls and other surfaces it is another source for loss of analyte e.g. by formation of volatile fluorine compounds or formation of analyte carrying aerosols. In some cases this problem can be overcome by the addition of boric acid and the resulting formation of tetrafluoroborate (BF_4^-). Tetrafluoroborate does not attack quartz and glass ware or silicon based adsorption materials such as normal or reversed phase materials for solid phase extraction (Boch et al. 2002) or application in chromatography.

In summary, the accuracy of trace and ultra-trace analysis of palladium in environmental samples stands and falls with collecting and measuring representative samples, which allow for an admissible extrapolation of the results and by performing reproducible digestion and enrichment procedures with high selectivity and highest possible enrichment of the analyte. Bearing this in mind the selection of a suitable quantification technique plays a subordinate but no less important role.

3 Selective Enrichment of PGM Using N,N-Dialkyl-N’-Benzoylthioureas

Coordination chemistry of platinum group metals is still a multifaceted and fascinating subject of current research e.g. in organometallic chemistry and in catalysis. From an analytical point of view the strong tendency especially of palladium to form very stable complex compounds with a variety of ligands is an interesting approach for the selective enrichment of palladium and other PGM from complex matrices. A ligand designed for this purpose should exhibit extraordinary high complex formation constants combined with a selective complexation behavior, high variability of the chemical and physicochemical properties of the ligand and the complexes to fine-tune polarity e.g. for phase transitions or optimized sorption behavior on stationary phases. A high chemical resistance against hydrolysis and oxidation is another prerequisite as traces of water soluble PGM species should be handled in acidic and oxidizing media to stabilize the analyte within the solutions.

In neutral or weakly acidic solutions colloidal PGM species can be formed by chemical reduction or formation of oxo-hydroxy compounds, which have a strong tendency to wall adsorption.

N,N-Dialkyl-N'-benzoylthioureas fulfil all of these requirements and were first utilized for selective PGM enrichment in 1985 and 1986 (König et al. 1985, 1986) followed by a series of investigations on the solvent extraction of PGM species (Vest et al. 1989, 1991) and patents e.g. (König et al. 1988, 1987). The chromatographic behavior of PGM and other complexes (König et al. 1984) as well as the crystal structure of N,N-Dialkyl-N'-benzoylthiourea complexes e.g. (Bensch and Schuster 1992) and fluorescence-labeled acylthiourea (Schuster and Unterreitmaier 1993, 1995) for fluorometric detection of heavy metals were subjects of further studies.

In 1996 the first fully automated enrichment and quantification system based on a flow injection (FI) approach utilizing N,N-Diethyl-N'-benzoylthiourea (DEBT) as a ligand for highly selective complexation of palladium was described in the literature (Schuster and Schwarzer 1996). It was intended for ultra-trace analysis of palladium in the lower ng·L^{-1} range from small sample volumes of 2−3 mL and provides an extraordinarily high overall selectivity with tolerance levels for commonly co-existing elements such as copper, nickel, cobalt, zinc and cadmium of up to 10 g L^{-1} and even more. Ubiquitous elements like iron and aluminum, earth alkaline and alkaline elements and others do not form stable complex compounds with DEBT in aqueous solutions. Due to the high chemical selectivity, it was even possible to measure palladium traces in ruthenium, rhodium, osmium, iridium, platinum, silver and gold standard solutions (c_{metal} = 1 g L^{-1}) intended for the use in atomic spectrometry. Validation was performed by recovery experiments in various matrices (98 ± 3 %) and by analysis of the reference material BCR-723 (found 6.0 ± 0.75 µg Pd kg^{-1}, certified value 6.0 ± 1.8 µg Pd kg^{-1}). Precision of the measurements is around 5 % in the lower ng L^{-1} range.

For determination GFAAS was chosen as it combines sufficient detection power, robustness and low operating costs for single element analysis. Small sample volumes of typically 20−40 µL applied by a high precision pipetting system is another advantage compared to sample introduction systems based on nebulizers which are much more susceptible to malfunction especially with regard to solvents with high viscosity/density and high concentrations of dissolved or dispersed analyte and/or matrix components. Volatilization of organic and other potentially interfering matrix constituents within the furnace temperature program is another pleasant tool provided by GFAAS. The flow injection system was also combined with Neutron Activation Analysis (NAA) to remove bromine and other elements which cause a strongly enhanced base line in the relevant energy range of the Pd-109 decay (Ag-109 m, 88.03 keV) (Schwarzer et al. 2000). With this setup it was possible to evaluate the palladium content in gasoline for the first time. Coupling of Electrothermal Atomization to Laser Absorption Fluorescence Spectrometry (ET LAFS) was performed for the determination of palladium in airborne particulate matter from Berlin, Germany (Tilch et al. 2000). In the meantime other research groups also utilized N,N-Dialkyl-N'-benzoylthioureas for trace analysis of PGM (Meeravali and Jiang 2008; Philippeit and Angerer 2001; Alshanaa and Aygüna 2011; Limbeck et al. 2004).

In the present work the determination of palladium in traffic related tunnel dust from the outer city ring of Munich utilizing the developed FI-GFAAS system and a specifically optimized digestion procedure (Boch et al. 2002) was continued and now includes the period from 1994 to 2012. For the determination of platinum in the same samples a new easy to perform separation and enrichment procedure based on cloud point extraction (CPE) with N,N-Di-(n-hexyl)-N'-benzoylthiourea (DHBT) as a selective reagent for complexation was used.

4 Selective Enrichment of Platinum Species by Ligand Supported Cloud Point Extraction

CPE is a very interesting analytical approach for trace metal enrichment as it combines high enrichment factors, a fast and easy assembly and the omission of (toxic) organic solvents (Pytlakowska et al. 2013). With N,N-Dialkyl-N'-benzoylthioureas as selective complexing agents CPE was first used for the decontamination of heavy metal polluted soils (Schuster et al. 1998). In aqueous solutions platinum occurs in two stable oxidation states Pt(II) and Pt(IV), normally existing as anionic complexes e.g. $[PtCl_4]^{2-}$ or $[PtCl_6]^{2-}$ which, depending on their concentration and chemical environment, have a strong tendency for ligand exchange reactions with small monodentate ligands (Al-Bazi and Chow 1984). After oxidizing digestion procedures Pt(IV) complex compounds are the dominating species, which show low reaction rates with N,N-Dialkyl-N'-benzoylthioureas at temperatures <40 °C. This is caused by a distinct kinetic inhibition of the complex formation (Vest et al. 1991) and allows for an effective separation of palladium traces from Pt(IV) containing solutions (König et al. 1988). To overcome the kinetic limitations tin(II) chloride ($SnCl_2$) is a good choice as it destabilizes Pt(IV) and also Rh(III) and Ir(III) species by the intermediate formation of $M[SnCl_3]_x$ complex compounds (Al-Bazi and Chow 1984) which in turn can be complexed by N,N-Dialkyl-N'-benzoylthioureas via ligand exchange. This ligand exchange is not kinetically limited and leads to the thermodynamically much more stable bidentate N,N-Dialkyl-N'-benzoylthiourea complex compounds. $SnCl_2$ also acts as a reducing agent, Pt(IV) can be reduced to Pt(II), a kinetically more labile species which forms very stable complex compounds with N,N-Dialkyl-N'-benzoylthioureas.

The enrichment procedure after sample digestion (Boch et al. 2002) and complex formation is easy to perform and utilizes the formation of micelles in surfactant containing aqueous solutions. N,N-Dialkyl-N'-benzoylthioureas, particularly those substituted with long alkyl chains like N,N-Di-n-hexyl-N'-benzoylthiourea (DHBT), form neutral, apolar complex compounds which can be effectively incorporated within micelles. Thermal induced coagulation of the micelles above the so called cloud point temperature leads to the formation of a surfactant rich phase which can easily be separated from the aqueous phase e.g. by centrifugation. The residual small surfactant droplet containing the platinum complex compounds is then dissolved in a small volume of a mixture of ethanol and hydrochloric acid and forwarded to GFAAS measurement without further treatment (Sievers and Schuster 2015). For platinum an enrichment factor of 60 and a limit of detection of 15 ng L^{-1} are achieved. Validation was performed by analysis of the reference materials BCR-723 (found 80.8 ± 3.87 µg Pt kg^{-1}, certified value 81.3 ± 3.3 µg Pt kg^{-1}) and SARM−7 (found 3.34 ± 0.44 mg Pt kg^{-1}, certified value 3.74 ± 0.045 mg Pt kg^{-1}). Precision is 5 % in the lower ng L^{-1} range.

5 Collection, Pretreatment and Matrix Characterization of the Tunnel Dust Samples

Tunnel dust samples were collected from the roofs of emergency call boxes in a height of about 2.3 m in three different tunnels (see introduction) and covered the years 1994, 1998, 2001, 2007, 2009, 2010 and 2012. After sampling the dust was completely removed from the roofs to avoid sampling of the same dust in subsequent years. The samples were dried for 24 h at 120 °C the gradual replacement and homogenized in a ball mill. Sieving of the collected dust was not necessary, since only small dust particles settle on the roofs of the boxes. Traffic statistics provided by the Department of Urban Planning and Building Regulation, City of Munich, Germany PLAN-HAI-31-1 are listed in Table 1.

Matrix characterization included quantification of relevant major, minor and trace elements. A selected compilation of elements is shown in the Figs. 1, 2 and 3. The major elements carbon, hydrogen, nitrogen, sulfur, and silicon were determined by elementary analysis. Other elements as well as minor and trace elements were determined by TXRF.

6 Results and Discussion

Matrix characterization of the main components carbon, hydrogen, nitrogen, sulfur, silicon, iron, zinc and calcium determined in road dust samples from 1994 to 2012 and 2001 to 2012 respectively show, apart from one noteworthy exception (sulfur) a quite constant composition. The sulfur content in the dust samples of all three

Table 1 Traffic-density monitored by the municipal administration of the city of Munich, Germany (average of vehicles within 24 h) in the city road tunnels "Landshuter Allee" "Candid" and "Trappentreu" from 1990 to 2007

Landshuter allee: vehicles 24 h^{-1}	Candid: vehicles 24 h^{-1}	Trappentreu: vehicles 24 h^{-1}
1992: 94,000	1990: 115,000	1991: 103,000
1994: 100,000	1996: 128,000	1994: 124,000
1997: 118,000	1997: 94,000	1998: 126,000
2005: 99,000	2007: 139,000	2007: 136,000
2007: 129,000	2011: 143,000	2011: 135,000

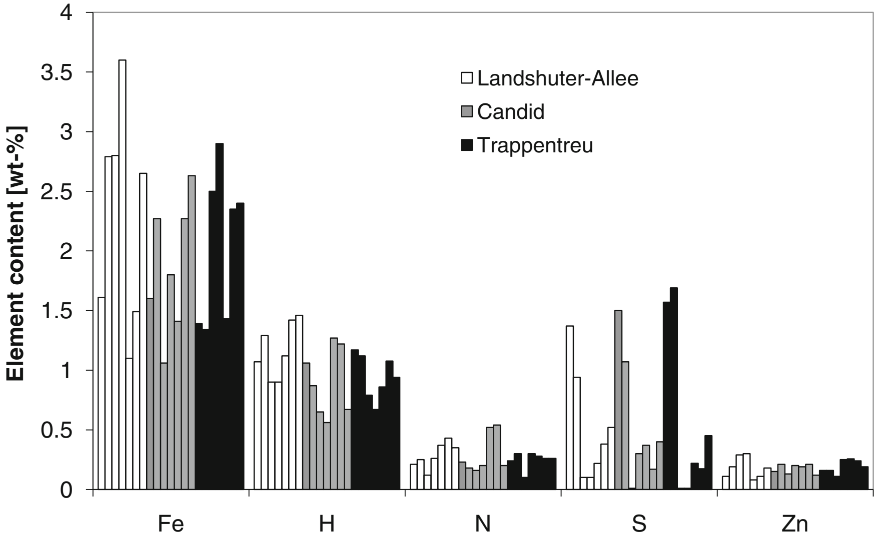

Fig. 1 Constituents of road dust of the years 1994, 1998, 2001, 2007, 2009, 2010 and 2012

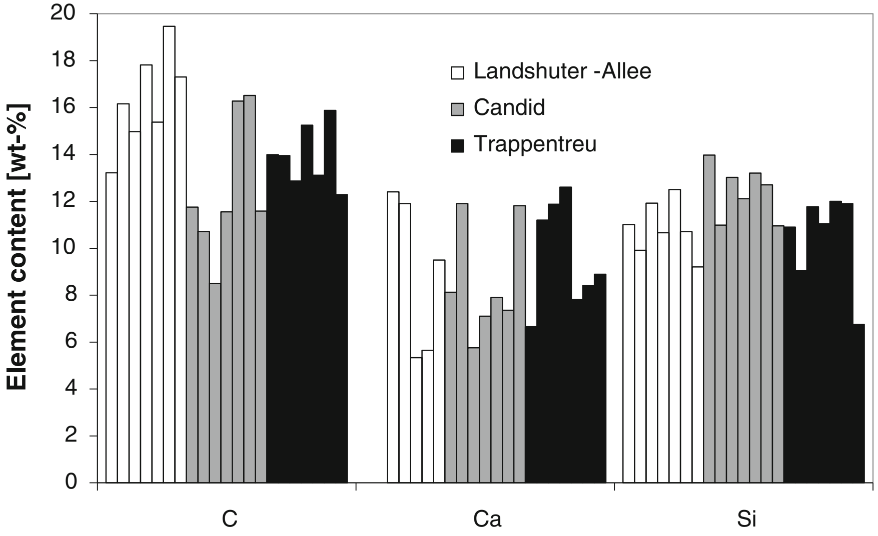

Fig. 2 Constituents of road dust of the years 1994, 1998, 2001, 2007, 2009, 2010 and 2012

tunnels decreased significantly in the years after 1998. This is most probably attributable to the legally required reduction of the sulphur content in gasoline and diesel fuels. The contents of the main components as well as the trace components chromium, copper and manganese reveal some fluctuations which are mostly of statistical nature but do not show a clear trend. These data support the assumption

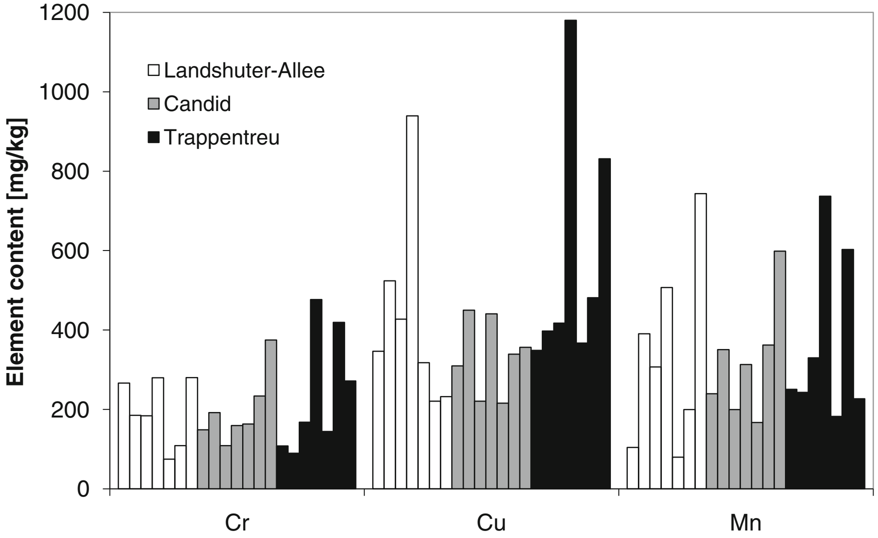

Fig. 3 Constituents of road dust of the years 1994, 1998, 2001, 2007, 2009, 2010 and 2012. Determination of Ca, Fe, Cr, Mn, Cu and Zn was performed by TXRF, other elements by elementary analysis

that the dust matrix remained constant over the years and that the sampling locations were well chosen to investigate long-term trends for ultra-trace elements like palladium or platinum.

The average palladium concentration in the dust samples increased significantly from 1994 (17.7 g Pd kg^{-1}) to 2007 (389 µg Pd kg^{-1}) were it reached a maximum. From 2009 onwards there was a steady decline in the average palladium concentration, reaching a minimum (236 µg Pd kg^{-1}) in 2012 (Fig. 4). The increase of the palladium concentration in the tunnel dust from 1994 to 2007 can easily be explained by the gradual replacement of platinum by palladium in automotive catalytic converters (Matthey 2012). In 2007 traffic density monitored by the municipal administration of the city of Munich also reached a high level which roughly remained the same up to today.

Platinum concentration in the dust samples increase between 1994 and 2001 and decline from 2001 to 2012 (Table 2). The increase in platinum content from 1994 to 2001 can be explained by the increasing use of automobile converters, promoted by the legislature. The decrease in the platinum content of the road dust samples since 2001 is mainly due to the replacement of platinum by palladium in the production of exhaust catalysts.The most likely explanation for the decline of the palladium and platinum concentration in the tunnel dust after 2007 is progress in the production of automotive catalytic converters and/or progress in automobile engine construction, a quite encouraging development, especially if taking into account that the pollutant emissions caused by traffic has also progressively been reduced.

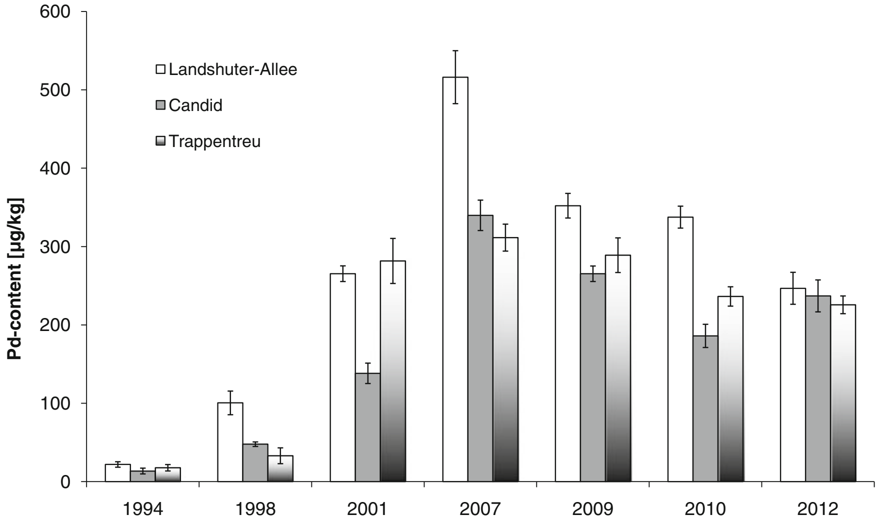

Fig. 4 Palladium content of road dust, determined by FI GFAAS (n = 3, error bar is the standard derivation of three independent samples)

Table 2 Platinum content of road dust, determined by GFAAS after CPE-enrichment (n = 3, error is the standard derivation of three independent samples)

	Landshuter allee	Candid	Trappentreu
	µg Pt kg^{-1}	µg Pt kg^{-1}	µg Pt kg^{-1}
1994	183.4 ± 16.3	–	182.7 ± 8.6
1998	306.4 ± 38.8	236.5 ± 45.8	251.4 ± 28.7
2001	641.9 ± 29.4	319.0 ± 14.8	543.9 ± 34.8
2007	308.4 ± 10.3	242.4 ± 7.2	269.6 ± 47.4
2009	–	255.3 ± 38.7	274.6 ± 29.8
2010	–	136.8 ± 28.6	172.1 ± 44.9
2012	143.2 ± 10.3	130.9 ± 21.7	126.8 ± 15.9

References

Aberer W, Holub H, Strohal R, Slavicek R (1993) Palladium in dental alloysthe dermatologists' responsibility to warn? Contact Dermatitis 28:163−165

Al-Bazi SJ, Chow A (1984) Platinum metals-solution chemistry and separation methods (ion-exchange and solvent extraction). A Chow, Talanta 31:815−836

Alshanaa U, Aygüna RS (2011) Determination of platinum and palladium in soil as their chelates with N, N-diethyl-N'-benzoylthiourea by RP-HPLC. J Liq Chromatogr Relat Technol 34:14

Barbante C, Veysseyre A, Ferrari C, Van de Velde K, Morel C, Capodaglio G, Cescon P, Scarponi G, Boutron C (2001) Greenland snow evidence of large scale atmospheric contamination for platinum, palladium, and rhodium. Environ Sci Technol 35:835−839

Bensch W, Schuster M (1992) Die Kristallstruktur von Tris(N, N-Diethyl-N'-benzoylthioureato) rhodium (III). Z Anorg Allg Chem 615:93

Boch K, Schuster M, Risse G, Schwarzer M (2002) Microwave-assisted digestion procedure for the determination of palladium in road dust. Anal Chim Acta 459:257−265

Jackson MT, Sampson J, Prichard HM (2007) Platinum and palladium variations through the urban environment: evidence from 11 sample types from Sheffield. UK Sci Tot Environ 385:117

Matthey J (2012) Platinum 2012 Interim Review

König K-H, Schuster M, Schneeweis G, Steinbrech B (1984) Zur Chromatographie von Metallchelaten XIV. Dünnschicht-Chromatographie von N, N-Dialkyl-N'-benzoylthioharnstoff-Chelaten. Fresenius Z Anal Chem 319:66

König K-H, Schuster M, Steinbrech B, Schneeweis G, Schlodder R (1985) N, N-Dialkyl-N' -benzoylthioharnstoffe als selektive Extraktionsmittel zur Abtrennung und Anreicherung von Platinmetallen. Fresenius Z Anal Chem 321:457

König K-H, Pletsch H-J, Schuster M (1986) N, N-Dialkyl-N'-benzoylharnstoffe als Fällungs- und Extraktionsreagenzien. Fresenius Z Anal Chem 325:621

König K-H, Schuster M, Hollmann D, Schlodder R (1988) Verfahren zur Abtrennung und Reinigung der Platingruppenmetalle. EP 144(566):B1

König K-H, Schuster M, Schneeweis G, Steinbrech B, Schlodder R (1987) Verfahren zur Abtrennung und Reinigung der Platingruppenmetalle. EP 144(565):B1

Kristine H, Morrison G, Rach S (2004) Environmental routes for platinum group elements to biological materials—a review. Sci Total Environ 334−335:21−38

Leopold K, Maier M, Weber S, Schuster M (2008) Long-term study of palladium in road tunnel dust and sewage sludge ash. Environ Pollut 156:341−347

Limbeck A, Rudolph E, Hann S, Koellensperger G, Stingeder G, Rendl J (2004) Flow injection on-line pre-concentration of platinum coupled with electrothermal atomic absorption spectrometry. J Anal At Spectrom 19:1474

Meeravali NN, Jiang S-J (2008) Interference free ultra-trace determination of Pt, Pd and Au in geological and environmental samples by inductively coupled plasma quadrupole mass spectrometry after a cloud point extraction. J Anal At Spectrom 23:854−860

Philippeit G, Angerer J (2001) Determination of palladium in human urine by high-performance liquid chromatography and ultraviolet detection after ultraviolet photolysis and selective solid-phase extraction. J Chromatogr B Biomed Sci Appl 760:237−245

Pytlakowska K, Kozik V, Dabioch M (2013) Complex-forming organic ligands in cloud-point extraction of metal ions: a review. Talanta 110:202−228

Rauch S, Hemond HF, Barbante C, Owari M, Morrison GM, Peucker-Ehrenbrink B, Wass U (2005) Importance of automobile exhaust catalyst emissions for the deposition of platinum, palladium, and rhodium in the Northern Hemisphere. Environ Sci Technol 39:8156−8162

Schäfer J, Hannker D, Eckhardt J-D, Stüben D (1998) Uptake of traffic-related heavy metals and platinum group elements (PGE) by plants. Sci Total Environ 215:59−67

Schuster M, Unterreitmaier E (1993) Fluorometric detection of heavy metals with pyrene substituted N-acylthioureas. Fresenius J Anal Chem 346:630

Schuster M, Schwarzer M (1996) Selective determination of palladium by on-line column preconcentration and graphite furnace atomic absorption spectrometry. Anal Chim Acta 328:1

Schuster M, Sandor K, Müller J (1998) Entfernung von Schwermetallen aus einem Boden mit hohem Schluffanteil. Umweltwiss Schadst Forsch 10:99−106

Schwarzer M, Schuster M, von Hentig R (2000) Determination of palladium in gasoline by neutron activation analysis and automated column extraction. Fresenius J Anal Chem 368:240−243

Sievers H, Schuster M (2015) Trace analysis of platinum in raod dust samples by cloud point extraction and GFAAS. Analytical and Bioanalytical Chemistry in preparation

Tilch J, Schuster M, Schwarzer M (2000) Determination of palladium in airborne particulate matter in a German city. Fresenius J Anal Chem 367:450−453

Unterreitmaier E, Schuster M (1995) Fluorometric detection of heavy metals with N-Methyl-N-9-(methylanthracene)-N'-benzoylthiourea. Anal Chim Acta 309:339

Vamnes JS, Lygre GB, Gronningsaeter AG, Gjerdet NR (2004) Four years of clinical experience with an adverse reaction unit for dental biomaterials. Commun Dent Oral Epidemiol 32:150−157

Vest P, Schuster M, König K-H (1989) Solventextraktion von Platinmetallen mit N-mono- und N, N-disubstituierten Benzoylthioharnstoffen. Fresenius Z Anal Chem 335:759

Vest P, Schuster M, König K-H (1991) Influence of tin(II) chloride on the solvent extraction of platinum group metals with N, N-di-n-hexyl-N'-benzoylthiourea. Fresenius J Anal Chem 339:142

Whiteley JD, Murry F (2005) Autocatalyst-derived platinum, palladium and rhodium (PGE) in infiltration basin and wetland sediments receiving urban runoff. Sci Total Environ 341:199−209

Zereini F, Zientek Ch, Urban H (1993) Konzentration und Verteilung von Platingruppenelementen (PGE) in Böden: Platinmetall-Emission durch Abrieb des Abgaskatalysatormaterials. Umweltwissenschaft und Schadstoff-Forschung 3:130−134

Zereini F, Skerstupp B, Urban H (1994) A Comparison between the use of sodium and lithium tetraborate in platinum-group elements determination by nickel sulphide fire-assay. Geostandards Newsletter 18:105−109

Zereini F, Wiseman C, Püttmann W (2007) Changes in palladium, platinum and rhodium concentrations and their spatial distribution in soils along a major highway in Germany from 1994 to 2004. Environ Sci Technol 41:451−456

Characterization of PGEs and Other Elements in Road Dusts and Airborne Particles in Houston, Texas

Shankararaman Chellam and Ayşe Bozlaker

Abstract It is imperative to quantify a wide range of elements in order to rigorously apportion the myriad sources of airborne particulate matter especially in industrialized urban environments. Herein, our recently reported analytical method that is optimized for the measurements of Rh, Pd, and Pt alongside numerous representative, transition, and lanthanoid elements is described. We also implemented the newly developed technique for the detailed elemental analysis of several tunnel dusts, surface road dusts, and airborne particulate matter collected in the greater Houston, Texas area. Rh, Pd and Pt were highly enriched in dusts swept from the road surface of the Washburn Tunnel averaging 152 ± 52, 770 ± 208 and 529 ± 130 ngg^{-1} respectively. Their concentrations were significantly lower in surface road dusts with Rh, Pd, and Pt ranging only between 5.9–8.4, 33.0–88.2, and 90.8–131 ngg^{-1}. Average Rh, Pd, and Pt concentrations in ambient aerosols were 1.5, 11.1, and 4.5 pgm^{-3} in $PM_{2.5}$ and 3.8, 23.1, and 15.1 pgm^{-3} in PM_{10}, respectively. Rh, Pd, and Pt levels were elevated in the air inside the Washburn Tunnel reaching 12.5, 91.1, and 30.1 pgm^{-3} in $PM_{2.5}$ and 36.3, 214, and 61.1 pgm^{-3} in PM_{10}, respectively. These are amongst the first such detailed measurements in the United States and represent our efforts to rigorously quantify particulate pollution emanating from light-duty vehicles.

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1 Background

Rh, Pd, and Pt are integral components of catalytic converters employed to reduce emissions of unburnt fuel, CO, and NOx from gasoline-driven light duty vehicles. High temperature abrasion and attrition releases a portion of these platinum group elements (PGEs) during vehicle operation making them important tracers of tailpipe emissions from light duty vehicles. Additionally, there is recent concern about potential PGE impacts on human health (Wiseman and Zereini 2009). Environmental colloids originate from a myriad number of sources each with substantially different characteristics. Therefore, to better understand their origins, behavior and transformations they undergo, it is important to quantify their composition in terms of a wide range of representative, transition, and lanthanoid elements. This chapter focuses on road dusts and aerosols, two important compartments of environmental PGEs. Most reports of the elemental composition of these particles have not reported Rh, Pd, and Pt because their detection at trace concentrations is typically very challenging (Chellam et al. 2005; Sternbeck et al. 2002). Others generally report two or three PGEs alone, or include a very limited number of other metals (e.g. Pb, Ni, Cu, Zn and Ce) along with PGEs (as summarized in Table 1). Consequently, we recently developed a novel sample preparation and inductively coupled plasma—mass spectrometry (ICP-MS) method for measuring numerous major and trace elements, including PGEs, in road dusts and atmospheric particulate matter (Spada et al. 2012).

To date, many reports have been published on PGE concentrations in airborne particulate matter and road dusts in Europe, Australia, and Asia. In contrast, relatively less is known about PGE concentrations in the United States. We Texans love our cars, having driven 33.9 million km in July 2013 within the state of Texas alone (FHWA 2013). Given the high vehicle-miles driven in Texas, we recently sampled fine and coarse aerosols in the Washburn Tunnel, which is the largest vehicular tunnel in the Southern United States and the only currently operating underwater vehicle tunnel in Texas (Bozlaker et al. 2014). The objective of this chapter is to present our sample extraction and analytical method along with a summary of our PGE measurements in airborne particulate matter and urban road dusts in Houston, Texas. We also provide a detailed review of the recent literature regarding analytical methods for PGE measurement as well as Rh, Pd, and Pt concentrations in relevant environmental compartments.

2 Analytical Method Development

2.1 Literature Review

Important details of PGE analytical techniques along with associated sample preparation methods published since the year 1999 are provided in Table 1. The purpose of this summary is to emphasize our assertion that earlier investigations

Table 1 Sample preparation and analysis methods used for determination of platinum group elements in environmental samples

Analytes	Sample type	Digestion method	Pre-concentration/ separation method for PGEs	Analysis method	SRM used	Reference
Rh, Pd, Pt and 48 other elements	Airborne $PM_{2.5}$, PM_{10}, road dust	1. MW-assisted digestion with aqua regia. 2. Separation of samples into two equal parts. 3. Evaporation of one part and dissolution of dry residues in HCl (PGEs). 4. MW-assisted digestion of second part in two stages with HF, then H_3BO_3 (non-PGEs)	Cation-exchange chromatography	DRC-q-ICP-MS	BCR 723 (200 mg); NIST SRM 2556, SRM 1648a (20 mg)	This study
Rh, Pd, Pt	Road dust	–	NiS fire assay	ICP-MS	BCR 723	(Pan et al. 2013)
Rh, Pd, Pt and Ir	Soil	–	NiS fire assay	ICP-MS	NIST SRM 2556, WMG-1, UMT-1	(Mihajevic et al. 2013)
Pd, Pt	Airborne $PM_{2.5}$, PM_{10}, TSP	1. MW-assisted digestion in two stages with HCl, HNO_3, and then HF. 2. Evaporation and dissolution of dry residues in aqua regia, then HCl	Cation-exchange chromatography, mathematical correction	ID-SF-ICP-MS	NIST SRM 2556	(Puls et al. 2012)
Rh, Pd, Pt	Airborne PM_1, $PM_{2.5}$, PM_{10}	1. High-pressure digestion with aqua regia. 2. HF treatment. 3. Evaporation and dissolution of dry residues in HNO_3, then HCl	Te and Hg co-precipitation	ID-q-ICP-MS for Pt and Pd; q-ICP-MS for Rh	BCR 723	(Zereini et al. 2012)

(continued)

Table 1 (continued)

Analytes	Sample type	Digestion method	Pre-concentration/ separation method for PGEs	Analysis method	SRM used	Reference
Pd and 37 other elements	Airborne $PM_{2.5}$	–	–	XRF	–	(Mancilla and Mendoza 2012)
Rh, Pd, Pt and 50 other elements	Airborne $PM_{0.1}$, $PM_{2.5}$, PM_{10}	MW-assisted digestion with HNO_3, HCl, HF	–	SF-ICP-MS	NIST SRMs 2556, 1649a, 2709	(Hays et al. 2011)
Rh, Pd, Pt and 16 other elements	Exhaust fumes	MW-assisted digestion with H_2O, HCl, HNO_3	Cation-exchange chromatography	ICP-MS	BCR 723 (50 mg)	(Cairns et al. 2011)
Rh, Pt and 40 other elements	Airborne $PM_{10–2.5}$	MW-assisted digestion with HNO_3, HCl, HF	–	SF-ICP-MS	NIST SRMs	(Pakbin et al. 2011)
Pd and 6 other elements	Airborne PM_{10}	1. High-pressure digestion with aqua regia. 2. HF treatment after evaporation. 3. Evaporation and dissolution of dry residues in HNO_3	Te and Hg co-precipitation	ID-q-ICP-MS	BCR 723 (500 mg); TDB-1, WPR-1 (200 mg)	(Alsenz et al. 2009)
Rh, Pd, Pt	Airborne TSP, soil, plant	–	NiS fire assay	ICP-MS	GBW 07294	(Pan et al. 2009)
Rh, Pd, Pt and Au	Road dust, road sweeper, gully	–	Pb fire assay for Pd, Pt, Au; NiS fire assay for Rh	ICP-MS	OREAS 13P, AMIS 0002, Garnet ST 321	(Prichard et al. 2009)

(continued)

Table 1 (continued)

Analytes	Sample type	Digestion method	Pre-concentration/ separation method for PGEs	Analysis method	SRM used	Reference
Rh, Pd, Pt and Pb	Road dust, soil	1. MW-assisted digestion in two steps with HNO_3, HF, then H_3BO_3. 2. Filtration. 3. Evaporation and dissolution of dry residues in HNO_3	–	GFAAS	BCR 723	(Tsogas et al. 2009)
Rh, Pd, Pt and Ir, Pb	Road dust	1. Open vessel digestion with aqua regia. 2. Evaporation and dissolution of dry residues in HCl. 3. Digestion with HCl, HNO_3, $HClO_4$, HF for Pb	Cation-exchange chromatography	ICP-MS	BCR 723 (100 mg), RM 8704 (500 mg)	(Sutherland et al. 2008)
Rh, Pd, Pt and 10 other elements	Road dust	MW-assisted digestion with aqua regia.	Cloud point extraction, mathematical correction	ICP-MS	–	(Simitchiev et al. 2008)
Rh, Pd, Pt and Ir	Road dust, soil, sediment	1. Open vessel digestion with aqua regia. 2. Evaporation and dissolution of dry residues in HCl	Cation-exchange chromatography	ICP-MS	BCR 723	(Sutherland et al. 2007)
Rh, Pd, Pt and 4 other elements	Road dust	1. Open vessel digestion with aqua regia. 2. Evaporation and dissolution of dry residues in H_2O	Mathematical correction	ICP-MS	–	(Wang et al. 2007)
Rh, Pd, Pt	Airborne TSP, soil	–	NiS fire assay	ICP-MS	–	(Wichmann et al. 2007)

(continued)

Table 1 (continued)

Analytes	Sample type	Digestion method	Pre-concentration/ separation method for PGEs	Analysis method	SRM used	Reference
Rh, Pd, Pt	Soil	–	NiS fire assay	GFAAS	–	(Zereini et al. 2007)
Rh, Pt	Airborne PM_{10}	1. MW-assisted digestion with HNO_3, HF, $HClO_4$. 2. Evaporation and dissolution of dry residues in HCl	–	SF-ICP-MS	–	(Bocca et al. 2006)
Rh, Pd, Pt and Ir, Os	Airborne PM_{10}	–	NiS fire assay	Magnetic sector ICP-MS	–	(Rauch et al. 2006)
Pd, Pt and 5 other elements	Road dust	1. MW-assisted digestion with aqua regia (alternatively with aqua regia, HF). 2. Evaporation and dissolution of dry residues in HCl	Cation-/anion-exchange chromatography, mathematical correction	q-ICP-MS, GFAAS	BCR 723, CW–7	(Lesniewska et al. 2006)
Rh, Pd, Pt and 5 other elements	Airborne PM_{10}	1. MW-assisted digestion with aqua regia. 2. Evaporation and dissolution of dry residues in HCl	NiS fire assay, mathematical correction	SF-ICP-MS, q-ICP-MS	BCR 723 (100–250 mg); TDB-1 and WGB-1 (4.6–6.9 g)	(Rauch et al. 2005)
Rh, Pd, Pt and 12 other elements	Airborne PM_{22}, PM < 10 μm in 9 size mode	1. High-pressure digestion with HCl, HNO_3. 2. HF, then HNO_3 treatment. 3. Evaporation and dissolution of dry residues in DI water	Hg coprecipitation	AdSV (Pt, Rh), TXRF (Pd), SF-ICP-MS (non-PGEs)	–	(Zereini et al. 2005)

(continued)

Table 1 (continued)

Analytes	Sample type	Digestion method	Pre-concentration/ separation method for PGEs	Analysis method	SRM used	Reference
Rh, Pd, Pt and 38 other elements	Airborne $PM_{2.5}$, PM_{10}, PM < 18 μm in 11 size mode	MW-assisted digestion with aqua regia, HF	–	ICP-MS (PGEs and 25 other elements); XRF (Al, Si, P, S, Cl, K, Ca, Sc, Ge, Se, Br, I, Ce)	NIST SRMs	(Lough et al. 2005)
Rh, Pd, Pt and 9 other elements	Roadside soil	–	NiS fire assay, Te coprecipitation	HR-ICP-MS (PGEs); INAA, XRF (non-PGEs)	IAEA Soil-7; CANMET WPR-1, UMT-1, TDB-1, WGB-1; IGGE GPt-3, GSS-2, GPt-4	(Morcelli et al. 2005)
Pd and 6 other elements	Road dust, roadside soil	1. MW-assisted digestion with aqua regia. 2. Evaporation and dissolution of dry residues in HCl	Displacement solid-phase extraction	ETAAS	GBW 07291, GBW 07293	(Fang et al. 2005)
Rh, Pd, Pt	Road dust, grass	For Rh, Pt: 1. MW-assisted digestion in two stages with aqua regia, then HF for road dust; with HNO_3, H_2O_2, then HF for plant. 2. Evaporation and dissolution of residues in HCl. For Pd: 1.High pressure digestion with HNO_3, HCl. 2. Open vessel digestion with HF. 3. Evaporation and dissolution of dry residues in HNO_3, then HCl	Hg coprecipitation, mathematical correction	HR-ICP-MS, q-ICP-MS (Rh, Pt); HR-ICP-MS, TXRF (Pd)	–	(Lesniewska et al. 2004)

(continued)

Table 1 (continued)

Analytes	Sample type	Digestion method	Pre-concentration/ separation method for PGEs	Analysis method	SRM used	Reference
Rh, Pd, Pt	Airborne PM_{22} and PM < 10 µm in 9 size mode	1. High-pressure digestion with HCl, HNO_3. 2. HF, then HNO_3 treatment. 3. Evaporation and dissolution of dry residues in DI water	Hg coprecipitation	AdSV (Pt, Rh); TXRF (Pd)	–	(Zereini et al. 2004)
Rh, Pd, Pt and 10 other elements	Road dust, plants	Road dust: 1. MW-assisted digestion with HCl, HNO_3, HF. 2. Evaporation and dissolution of residues in HCl, HNO_3. Plants: MW-assisted digestion with HCl, HNO_3, HF	Isolation of Pd using its DDTC complex/anion-exchange chromatography, mathematical correction	q-ICP-MS, ICP-AES	SARM-7, JSd-2	(Djingova et al. 2003a)
Rh, Pd, Pt and 10 other elements	Airborne PM_{10}, road dust	1. MW-assisted digestion in two stages with aqua regia, then HF. 2. Evaporation and dissolution of dry residues in HCl. 3. For road dust, additional MW digestion with HF before evaporation	Te coprecipitation, mathematical correction	q-ICP-MS	CW-7, CW-8 (200 mg)	(Gomez et al. 2003)
Rh, Pd, Pt and 3 other elements	Airborne TSP, PM < 10 µm in 6 size mode	1. MW-assisted digestion with aqua regia, HF. 2. Open vessel digestion with $HClO_4$, then aqua regia. 3. Dissolution of dry residues in HCl	Anion-exchange chromatography	SF-ICP-MS	BCR 723 (100 mg), TM-27.2	(Kanitsar et al. 2003)

(continued)

Table 1 (continued)

Analytes	Sample type	Digestion method	Pre-concentration/ separation method for PGEs	Analysis method	SRM used	Reference
Rh, Pd, Pt and 4 other elements	Road dust, roadside soil	1. MW-assisted digestion with aqua regia. 2. Filtration of samples through 0.45 μm membrane filter. 3. Evaporation and dissolution of dry residues in HCl. 4. Alternatively, after MW digestion with aqua regia, open vessel digestion with HF/HNO_3, evaporation and dissolution of dry residues in HCl	Cation-exchange chromatography	q-ICP-MS	BCR 723	(Whiteley and Murray 2003)
Rh, Pd, Pt	Airborne $PM_{2.5}$, PM_{10}, PM < 10 μm in 7 size mode, PM < 65.3 μm in 5 size mode, TSP, road dust	1. MW-assisted or high-pressure digestion with aqua regia; aqua regia, HF; aqua regia, $HClO_4$ or aqua regia, HF, $HClO_4$. 2. Dilution with HCl	Mathematical correction	q-ICP-MS, SF-ICP-MS, DP-CSV	NIST SRM 2557, IMEP-11	(Gomez et al. 2002)
Rh, Pd, Pt	Road dust, sediment, car exhaust PM	1. MW-assisted digestion with aqua regia. 2. Evaporation and dissolution of dry residues in HCl	Te coprecipitation (sediment), mathematical correction	LA-ICP-MS	–	(Rauch et al. 2002)
Rh, Pd, Pt and Ru	Road dust, car exhaust PM	MW-assisted digestion with HNO_3, HF, $HClO_3/HClO_4$	Electrochemical preconcentration	ETAAS	CW-7, CRM NIES No. 8 (100 mg)	(Matusiewicz and Lesinski 2002)

(continued)

Table 1 (continued)

Analytes	Sample type	Digestion method	Pre-concentration/ separation method for PGEs	Analysis method	SRM used	Reference
Rh, Pd, Pt	Soil	1. Digestion with HNO_3, HCl, HF. 2. Evaporation and dissolution of dry residues in aqua regia. 3. Filtration of samples through 0.45 μm PTFE-filter. 4. Evaporation and dissolution of dry residues in aqua regia, then HNO_3	Te coprecipitation	ICP-MS	WPR-1	(Morton et al. 2001)
Rh, Pd, Pt	Airborne PM_{10}	1. MW-assisted digestion with aqua regia. 2. Evaporation and dissolution of dry residues in HCl	Mathematical correction	ICP-MS	NIST SRM 2557	(Rauch et al. 2001)
Rh, Pt	Airborne PM < 10 μm in 9 size mode, TSP	High-pressure digestion with HNO_3, HCl	–	AdSV	–	(Zereini et al. 2001a)
Ph, Pd, Pt and 8 other elements	Roadside soil, grass	1. High pressure digestion in two stages with HF, HNO_3, then aqua regia. 2. Evaporation and dissolution of residues in HCl	Cation-exchange chromatography	USN-ICP-MS	UMT-1	(Ely et al. 2001)
Ph, Pd, Pt	Road dust	MW-assisted digestion with aqua regia	–	LA-ICP-MS, HR-SF-ICP-MS	NIST SRM 2557 (50 mg)	(Motelica-Heino et al. 2001)

(continued)

Table 1 (continued)

Analytes	Sample type	Digestion method	Pre-concentration/ separation method for PGEs	Analysis method	SRM used	Reference
Rh, Pt and 7 other elements	Airborne PM_{10}, $PM < 10$ µm in 7 size mode, $PM < 65.3$ µm in 5 size mode, TSP, road dust	1. High pressure digestion in two stages with aqua regia, then HF. 2. Evaporation and dissolution of dry residues in HCl. 3. For road dust, additional digestion with HF before evaporation	Mathematical correction	q-ICP-MS	NIST SRM 2557	(Gomez et al. 2001)
Ph, Pd, Pt and 7 other elements	Airborne PM_{10}	1. MW-assisted digestion in two stages with aqua regia, then HF. 2. Evaporation and dissolution of dry residues in HCl	Mathematical correction	q-ICP-MS	NIST SRM 2557, IMEP-11	(Gomez et al. 2000)
Ph, Pd, Pt and 12 other elements	Road dust	Mineralization with HF	Mathematical correction	ICP-AES, ICP-MS, HR-ICP-MS, ETAAS (PGEs); XRF (non-PGEs)	–	(Schramel et al. 2000)
Rh, Pd, Pt	Airborne PM_{10}, road dust	1. MW-assisted digestion with aqua regia, HF. 2. Evaporation and dissolution of dry residues in HCl	Mathematical correction	HR-SF-ICP-MS	–	(Petrucci et al. 2000)
Rh, Pd, Pt	Road dust	1. MW-assisted digestion with aqua regia, HF. 2. Open vessel digestion with aqua regia. 3. Evaporation and dissolution of dry residues in HCl	Mathematical correction	SF-ICP-MS	CANMET WPR-1	(Kollensperger et al. 2000)

(continued)

Table 1 (continued)

Analytes	Sample type	Digestion method	Pre-concentration/ separation method for PGEs	Analysis method	SRM used	Reference
Rh, Pd, Pt and 8 other elements	Airborne TSP, soil, road dust, sewage sludge, incineration ash	Wet chemical digestion	Te coprecipitation (TSP), NiS fire-assay (other samples)	q-ICP-MS, GFAAS	SARM-7, WPR-1	(Schafer et al. 1999)
Rh, Pd, Pt and 6 other elements	Car exhaust fumes	1. MW-assisted digestion in two steps with aqua regia, then HF. 2. Evaporation and dissolution of residues in HCl. 3. Alternatively, MW-assisted digestion in two stages with H_2O, HNO_3, HCl, HF, then H_3BO_3	Mathematical correction	q-ICP-MS	NIST SRM 2557	(Moldovan et al. 1999)
Rh, Pd, Pt and Ru, Ir, Au	Soil, grass	1. High pressure digestion in two stages with HF, HNO_3, then aqua regia. 2. Evaporation and dissolution of residues in HCl	Cation-exchange chromatography	USN-ICP-MS	UMT-1	(Ely et al. 1999)

Abbreviations *TSP* Total suspended particles; *MW* Microwave; *ICP-MS* Inductively coupled plasma-mass spectrometry; *DRC* Dynamic reaction cell; *q* Quadrupole; *SF* Sector field; *HR* High resolution; *USN* Ultrasonic nebulization; *ID* Isotope dilution; *LA* Scanning laser ablation; *AES* Atomic emission spectroscopy; *XRF* X-ray fluorescence; *TXRF* Total reflection XRF; *GFAAS* Graphite furnace atomic absorption spectrometry; *FAA* Flame atomic absorption; *ETAAS* Electrothermal atomic absorption spectrometry; *INNA* Instrumental neutron activation analysis; *AdSV* Adsorptive voltammetry; *DP-CSV* Differential-pulse cathodic stripping voltammetry have largely optimized methods to extract and analyze Rh, Pd, and Pt along with a limited number of non-PGEs. It is again emphasized that it is necessary to measure PGEs along with numerous representative elements, transition metals, and lanthanoids in order to identify sources of different particles found in the urban atmosphere and road dusts.

2.2 Samples

2.2.1 Tunnel and Road Dust

The Washburn Tunnel (latitude + 29.733; longitude-95.211) connects the Houston suburbs of Galena Park and Pasadena. This underwater tunnel has two lanes of traffic in a 895 m long single-bore 20.7 m below the Ship Channel (Fig. 1). It is used daily by approximately 20,000 predominantly single-axle, gasoline-driven light duty vehicles at average speeds of 55–75 km/h. Positive air pressure is applied by two blowers located at the top of the tunnel at the north entrance. A backup fan is also available. These fans are designed to minimize carbon monoxide levels in the tunnel air by providing complete air exchange in less than 2 min.

Tunnel dust material was collected from three locations of a catwalk (~1.2 m elevation) near the north, middle and south ends and from the gutter (~5 cm below the road surface) near the middle of the tunnel. Road dust was also collected alongside three major surface roadways in Houston including (a) near the northern entrance of the Washburn Tunnel; (b) beneath an overpass at the intersection of three major highways (Interstate 69, Interstate 45 and State Highway 288); and (c) a Metropolitan Transit Authority transit center. Samples were dried at 105 °C for 24 h and sieved through 0.710 mm and 0.106 mm meshes prior to digestion. Electron micrographs of our road dust samples (Fig. 2) were qualitatively similar to other

Fig. 1 General view inside the Washburn Tunnel in Houston, TX at night time in the absence of vehicular traffic

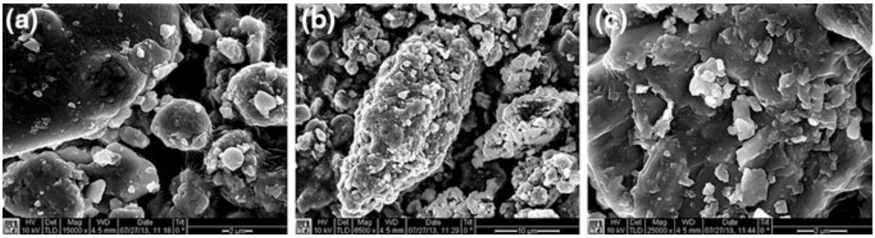

Fig. 2 Electron micrographs showing irregular morphology and grain size distribution of dusts

PGE-bearing road dusts (Prichard and Fisher 2012), showed their inherent heterogeneity and their wide particle size distribution. More details can be obtained from our recent paper (Spada et al. 2012).

2.2.2 Airborne Particulate Matter

Airborne $PM_{2.5}$ and PM_{10} in the tunnel were sampled on 47 mm Teflon filters using Rupprecht and Patachnick 2,025 Partisol samplers (1 m^3 h^{-1}) placed on the catwalk approximately 44 m from the north end. Background $PM_{2.5}$ and PM_{10} from the tunnel ventilation air supply were also collected from the intake area of the fan building, which is open to the ambient environment. Two sets of time-integrated PM samples were collected each encompassing 3–4 week periods between November 2, 2012 and January 2, 2013 to obtain sufficient PM mass in order to detect as many elements as possible above the sensitivity of ICP-MS. Sixteen representative elements (Li, Be, Mg, Al, Si, K, Ca, Ga, As, Rb, Sr, Sn, Sb, Cs, Ba, Pb), 17 transition metals (Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Mo, Rh, Pd, Cd, W, Pt) and 15 lanthanoids/actinides (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu, Th, U) were quantified.

2.2.3 Vehicle Autocatalyst

A composite sample of numerous regenerated autocatalysts representing multiple manufacturers, model types, and different PGEs loadings was obtained from Engelhard Corporation (currently BASF). Their Rh, Pd, and Pt concentrations were measured as 184, 1,148, and 814 $\mu g g^{-1}$, respectively.

2.2.4 Reference Materials

European Commission road dust BCR 723 (Rh, Pd, and Pt = 12.8, 6.1, and 81.3 $\mu g kg^{-1}$, respectively); NIST used auto catalyst SRM 2556 (Rh, Pd and Pt = 51.2, 326.0, and 697.4 $\mu g g^{-1}$, respectively); and NIST urban particulate matter SRM 1648a (no certified PGEs) were used for quality control.

2.3 Sample Preparation

A multi-step procedure including closed vessel microwave-assisted acid digestion, evaporation, and matrix separation using ion-exchange was developed for elemental extraction. Ion-exchange has been employed before by others to prepare samples for PGE analysis (Cairns et al. 2011; Dubiella-Jackowska et al. 2007; Kovacheva and Djingova 2002). The performance of both anion-exchange resin (Eichrom I-X8 100–200 mesh) and cation-exchange resin (Dowex 50WX8 200–400 mesh) was examined for the chemical separation of PGEs from the matrix components on chromatography column. Poor recoveries of PGEs, especially for Pd, were observed with anion-exchange, and consequently the analytical procedure was optimized with cation-exchanger to reduce potential isobaric and polyatomic spectral interferences (see Sect. 2.3.2) as used by others (Cairns et al. 2011; Ely et al. 1999; Lesniewska et al. 2006; Mukai et al. 1990).

Figure 3 is a flow chart illustrating sample preparation steps to extract metals prior to DRC-q-ICP-MS analysis (Spada et al. 2012). We found that chemical separation of samples with cation-exchange resin after digestion with aqua regia

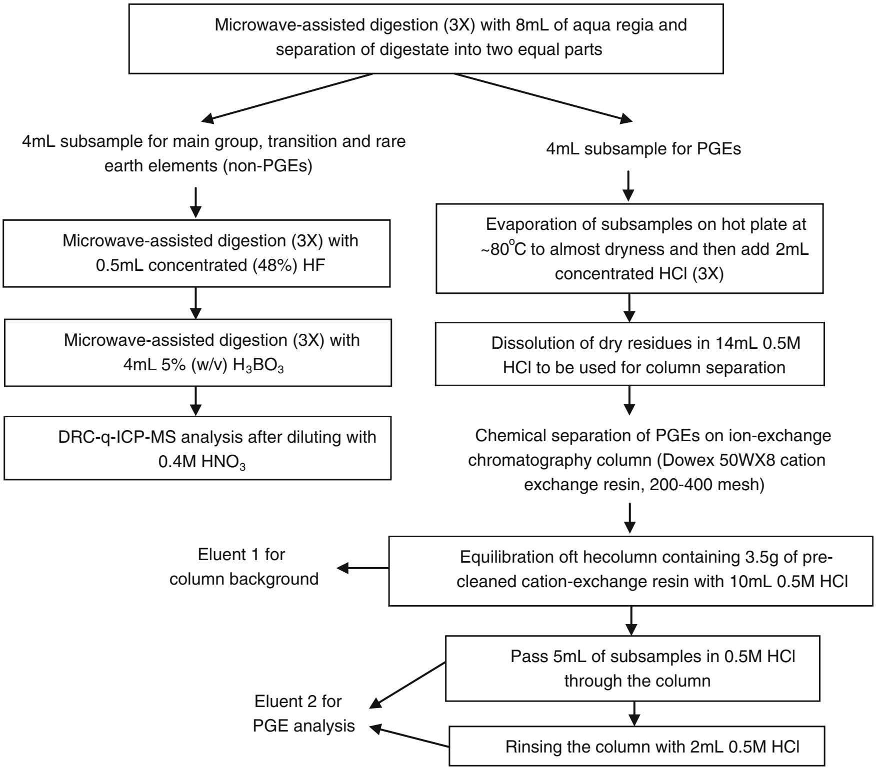

Fig. 3 Flow chart illustrating sample preparation steps prior to DRC-q-ICP-MS analysis

and HF resulted in poor recoveries for PGEs as reported earlier by others (Lesniewska et al. 2006). Therefore, after extraction with aqua regia, samples were separated into two equal parts based on the elements of interest. PGE subsamples were evaporated and cation-exchanged. Subsamples for all other elements were digested in two more stages, first with HF and then with H_3BO_3.

2.3.1 Closed Vessel Microwave-Assisted Acid Digestion

Digestion was performed in a programmable 1200 W microwave system (MARS 5, CEM Corp.) using 100 mL Teflon-lined vessels (HP-500 Plus, CEM Corp.) with set points of 200 °C and 300 psig and a 20 min dwell time. Digestion was controlled by a master vessel assembly equipped with pressure and temperature sensors. Our previously developed microwave-assisted acid digestion procedure (Danadurai et al. 2011; Kulkarni et al. 2007a, c) served as the basis for this work. First 2 mL HNO_3 (65 % EMD Chemicals) and 6 mL HCl (32–35 %, Optima) were added to each sample (200 mg for road/tunnel dust and BCR 723; 20 mg for SRMs 2556 and 1648a) in loosely capped Teflon vessels for 5 min. After three digestions in aqua regia at 300 psig and 200 °C for 20 min, 4 mL of subsamples were transferred to another vessel for additional PGE sample preparation. Secondly, 0.5 mL of HF (48 %, Fluka) was added to the remaining 4 mL digestate to completely digest siliceous material and the samples were digested three more times. Thirdly, 4 mL of 5 % (w/v) H_3BO_3 (99.99 %, Acros Organics) was added to each vessel to mask free fluoride ions in the solution and re-dissolve fluoride precipitates, which is especially important for lanthanoids. Samples were digested three more times at the same microwave settings. PGE subsamples were evaporated to near-dryness at approximately 80 °C, treated with 2 mL of concentrated HCl and reheated to near-dryness. This process was repeated twice to achieve near quantitative extraction and to remove HNO_3. The ultimate dry residues were dissolved in 14 mL of 0.5 M HCl before cation-exchange.

Figure 4 is a temperature and pressure profile of a sample matrix consisting of 6 mL HNO_3, 2 mL HCl, 1 mL HF, and 200 mg road dust in the master vessel. The pressure inside the digestion vessels increased due to contributions from vapor pressure of acids employed along with gaseous decomposition products generated during the digestion process (e.g., NOx, CO_2, SiF_4, SiF_6, etc.) (Kingston and Haswell 1997). Importantly, the pressure set-point of 300 psig was never reached demonstrating the elimination of potential runaway reactions by temperature feedback control. Monitoring the pressure/temperature during digestion showed that in all cases the control vessel was properly sealed and temperature was always the controlling parameter. A colorless solution was always obtained at the end of digestion demonstrating complete dissolution of particulate matter.

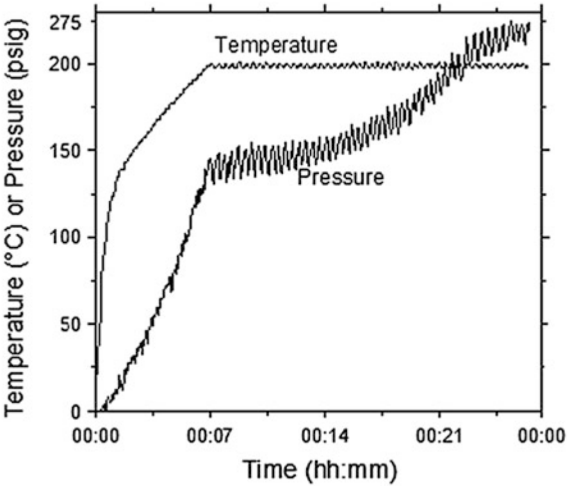

Fig. 4 Typical reaction profile for the microwave digestion of road dust using aqua regia and HF

2.3.2 Separation of Matrix Ions by Cation-Exchange Chromatography

The Dowex resin was ultrasonically cleaned using a mixture of 30 % (v:v) HCl and 1 % (v:v) HF (1 time), 4 M HCl (6 times), ultrapure water (twice), and 0.5 M HCl (twice) for 20 min each in series. Each Poly-Prep chromatography column (9 cm high, 2 mL resin bed volume (0.8 × 4 cm) with 10 mL reservoir, Bio-Rad) was packed with 3.5 g of cleaned resin and first equilibrated with 10 mL of 0.5 M HCl. The eluent was collected in a polyethylene tube to serve as the column background sample. More information on the operation of the cation exchange column can be found in our recent publication (Spada et al. 2012).

2.4 Analyte Quantification

Pt, Pd and Rh were measured along with representative elements (Li, Be, Mg, Al, Si, K, Ca, Ga, As, Se, Rb, Sr, Sn, Sb, Cs, Ba, Pb), transition metals (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Mo, Cd, W) and lanthanoids/actinides (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th, U) with a DRC-q-ICP-MS (ELAN DRCII, PerkinElmer). Instrumental settings and operating conditions were similar to our earlier work (Danadurai et al. 2011) except $0.2 \leq NH_3$ flow rate ≤ 1.0 $mLmin^{-1}$ and $0.25 \leq RPq \leq 0.8$. Standard solutions were freshly prepared by diluting single-element stock solutions in 0.4 M HNO_3. Internal standardization was done with 20 μgL^{-1} ^{74}Ge, ^{115}In, and ^{209}Bi.

Isotopic abundances of Rh, Pd, and Pt are summarized in Table 2 (Alsenz et al. 2009; Djingova et al. 2003a; Ely et al. 1999; Kollensperger et al. 2000; Simitchiev et al. 2008). As seen, major PGE interferences include ^{63}Cu, ^{65}Cu, ^{68}Zn, ^{85}Rb, ^{88}Sr,

Table 2 PGE isotopes and potential spectral interferences

Isotope (Natural abundance, %)	Interferent species[a]
^{103}Rh (100)	^{87}Rb^{16}O^{+}, ^{40}Ar^{63}Cu^{+}, ^{36}Ar^{67}Zn^{+}, ^{87}Sr^{16}O^{+}, ^{86}Sr^{17}O^{+}, ^{86}Sr^{16}O^{1}H^{+}, ^{66}Zn^{37}Cl^{+}, ^{68}Zn^{35}Cl^{+}, ^{206}Pb^{2+}
^{102}Pd (1.02)	^{86}Sr^{16}O^{+}, ^{204}Hg^{2+}, ^{204}Pb^{2+}, ^{102}Ru
^{104}Pd (11.14)	^{40}Ar ^{64}Zn^{+}, ^{88}Sr ^{16}O^{+}, ^{208}Pb^{2+}, ^{104}Ru
^{105}Pd (22.33)	^{40}Ar^{65}Cu^{+}, ^{36}Ar^{69}Ga^{+}, ^{89}Y^{16}O^{+}, ^{88}Sr^{17}O^{+}, ^{87}Sr^{18}O^{+}, ^{88}Sr^{16}O^{1}H^{+}, ^{87}Rb^{18}O^{+}, ^{68}Zn^{37}Cl^{+}, ^{70}Zn^{35}Cl^{+}, ^{35}Cl$_{3}^{+}$
^{106}Pd (27.33)	^{40}Ar ^{66}Zn^{+}, ^{90}Zr^{16}O^{+}, ^{89}Y^{16}O^{1}H^{+}, ^{106}Cd^{+}
^{108}Pd (26.46)	^{40}Ar ^{68}Zn^{+}, ^{38}Ar ^{70}Zn^{+}, ^{92}Zr^{16}O^{+}, ^{92}Mo^{16}O^{+}, ^{108}Cd^{+}
^{110}Pd (11.72)	^{40}Ar ^{70}Zn^{+}, ^{94}Zr^{16}O^{+}, ^{94}Mo^{16}O^{+}, ^{40}Ar ^{70}Ge^{+}, ^{110}Cd^{+}
^{190}Pt (0.01)	^{174}Yb^{16}O^{+}, ^{190}Os
^{192}Pt (0.78)	^{176}Hf^{16}O^{+}, ^{174}Yb^{18}O^{+}, ^{176}Lu^{16}O^{+}, ^{192}Os
^{194}Pt (32.97)	^{178}Hf^{16}O^{+}, ^{177}Hf^{17}O^{+}, ^{176}Hf^{18}O^{+}, ^{176}Yb^{18}O^{+}, ^{176}Lu^{18}O^{+}
^{195}Pt (33.83)	^{179}Hf^{16}O^{+}, ^{178}Hf^{17}O^{+}, ^{177}Hf^{18}O^{+}
^{196}Pt (25.24)	^{180}Hf^{16}O^{+}, ^{196}Hg
^{198}Pt (7.16)	^{182}W^{16}O^{+}, ^{198}Hg

[a] from (Alsenz et al. 2009; Djingova et al. 2003a; Ely et al. 1999; Kollensperger et al. 2000; Simitchiev et al. 2008)

^{89}Y, ^{90}Zr, ^{178}Hf, ^{179}Hf, and ^{206}Pb, which are also present in urban aerosols especially in industrialized areas (Moreno et al. 2010; Kulkarni et al. 2007b).

2.4.1 Cation-Exchange Column Performance

Major PGE interferences were measured in the column effluent and influent (see Fig. 3) for freshly prepared samples of BCR 723 and tunnel dust. As seen in Fig. 5, interferents concentrations decreased by approximately two orders of magnitude similar to previous reports (Cairns et al. 2011; Ely et al. 1999, 2001; Mukai et al. 1990). Interferences from the sample matrix were successfully reduced by 90.5–99.8 %, allowing quantitative recoveries for ^{103}Rh, ^{105}Pd, and ^{195}Pt from BCR 723 (i.e. 100.8 ± 6.5 %, 91.3 ± 10.3 %, and 97.8 ± 2.9 % respectively), demonstrating the suitability of the cation-exchange procedure for PGEs determination.

2.5 DRC Optimization

Table 3 summaries the potential mass spectrum interferences on important anthropogenic elements such as As, Zn, V, Ni, Cd. The corresponding reaction cell parameters and comparison of performance measures between the "standard"

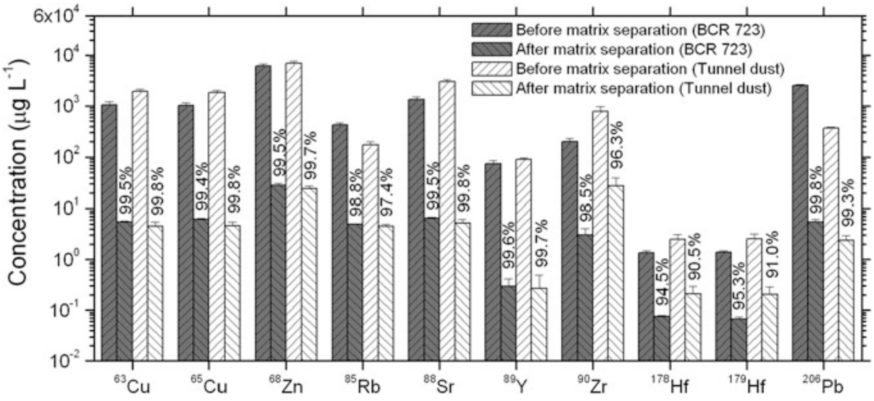

Fig. 5 Removal of major PGE interferents by cation-exchange. Average influent and effluent concentrations and removal percentages are shown for each element measured in BCR 723 (n = 3) and Washburn Tunnel dust samples (n = 3). Error bars correspond to one standard deviation

(i.e. no cell gas) and “DRC” (i.e. using a cell gas) modes of operation are also given. Removal of interferences that are caused by plasma (i.e. argon) and digestion sample matrix-based isobaric and polyatomic species at the same mass/charge ratio (m/z) of the analyte was necessitated especially following the use of aqua regia for sample digestion. This was accomplished using NH_3 as a reaction gas to facilitate ion-molecule collisions in a reaction/collision cell before ions entered the mass analyzer. This improved detection limits and decreased background equivalent concentrations (D’Ilio et al. 2011).

2.5.1 NH_3 Flow Rate Optimization

Background equivalent concentrations (BECs) for spiked samples were measured as a function of the NH_3 flow rate at a fixed RPq value of 0.45. Changes in BECs by varying NH_3 gas flow rate between 0 and 1 mLmin^{-1} are illustrated in Fig. 6 where zero cell gas flow indicates standard mode of operation. As seen, BECs decreased for several elements including As, Zn, V, Ni, and Cd using NH_3 in a range of flow rates (0.25–0.80 mLmin^{-1}).

Improvements in elemental detection can be attributed to removal of interferences through charge exchange, condensation and clustering reactions between NH_3 and the ion beam in the reaction cell. Interfering species can be converted into either neutral species or species with a new mass-to-charge ratio (m/z) that are different from the analyte by reacting with the cell gas. Alternately, reactions solely between the analyte and the cell gas produce new polyatomic species at m/z ratios free from interferences (Simpson et al. 2001). The capability of NH_3 to reduce spectral interferences is mainly due to the neutralization of interfering ions (A^+) by charge exchange reactions (D’Ilio et al. 2011; Tanner et al. 2000, 2002): $A^+ + NH_3$

Table 3 Summary of dynamic reaction cell (DRC) measurements

Element	Major polyatomic interferences[a]	DRC parameters		Method detection limit (μg L^{-1})		Accuracy with BCR 723 (μg g^{-1})		Accuracy with SRM 1648a (μg g^{-1})	
		NH$_3$ flow rate (mL min^{-1})	RPq value	Standard mode	DRC mode	Our study	Indicative value	Our study	Certified value
^{51}V	$^{35}Cl^{16}O^{+}$, $^{37}Cl^{14}N^{+}$, $^{36}Ar^{15}N^{+}$, $^{36}Ar^{14}N^{1}H$, $^{40}Ar^{11}B^{+}$, $^{34}S^{16}O^{1}H^{+}$, $^{102}Ru^{2+}$	0.80	0.65	2.08	0.48	82 ± 10	75 ± 2	130 ± 12	127 ± 11
^{60}Ni	$^{44}Ca^{16}O$, $^{25}Mg^{35}Cl$, $^{23}Na^{37}Cl$, $^{36}Ar^{24}Mg$, $^{120}Sn^{2+}$	0.35	0.80	2.67	2.52	161 ± 26	171 ± 3	76 ± 9	81 ± 7
^{64}Zn	^{64}Ni, $^{48}Ti^{16}O$, $^{48}Ca^{16}O$, $^{31}P^{16}O_{2}$, $^{32}S^{16}O_{2}$, $^{27}Al^{37}Cl$, $^{32}S_{2}$, $^{31}P^{16}O^{1}_{2}H$, $^{40}Ar^{14}N_{2}$, $^{40}Ar^{24}Mg$	0.60	0.40	28.01	14.91	1,462 ± 110	1,660 ± 100	5416 ± 161	4,800 ± 270
^{75}As	$^{40}Ar^{35}Cl$, $^{59}Co^{16}O$, $^{38}Ar^{1}_{2}H$, $^{36}Ar^{39}K$, $^{43}Ca^{16}O_{2}$, $^{23}Na^{12}C^{40}Ar$, ^{12}C $^{31}P^{16}O_{2}$, $^{40}Ca^{35}Cl$, Sm^{2+}, Nd^{2+}	0.25	0.50	5.16	0.46	19 ± 4	–	118 ± 9	116 ± 4
^{112}Cd	$^{96}Mo^{16}O$, $^{94}Zr^{17}O^{1}H$	0.80	0.60	0.027	0.040	2.5 ± 0.4	2.5 ± 0.4	74 ± 4	74 ± 2

[a] from (Danadurai et al. 2011; D'Ilio et al. 2011; Olesik and Jones 2006)

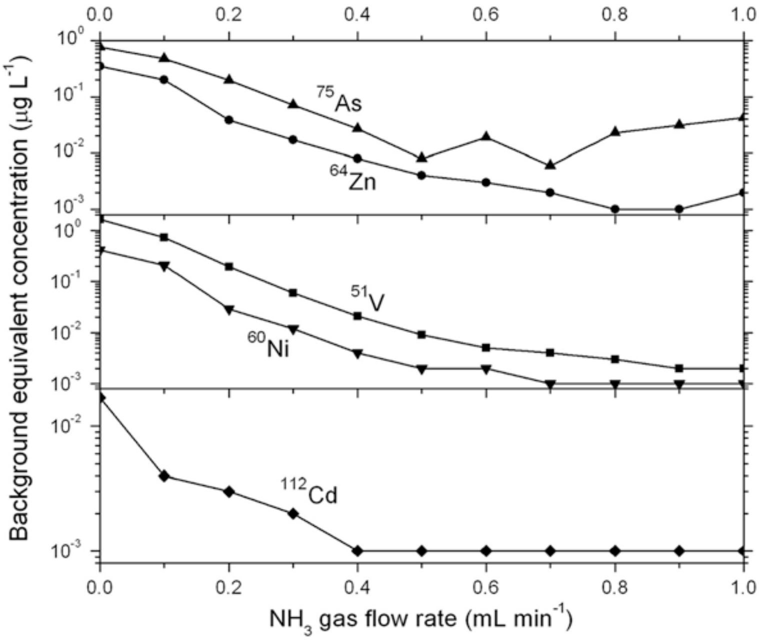

Fig. 6 Optimization of NH_3 gas flow rate for ^{75}As, ^{64}Zn, ^{51}V, ^{60}Ni, and ^{112}Cd. No cell gas indicates standard mode of operation

→ NH_4^+ + A (e.g., A = Se^+, Cr^+, V^+, Zn^+, $^{40}Ar\ ^{35}Cl^+$ on $^{75}As^+$, $^{40}Ar^{12}C^+$ and $^{37}Cl^{15}O^+$ on $^{52}Cr^+$, $^{40}Ar^{16}O^+$ on ^{56}Fe + , $^{35}Cl^{16}O^+$ and $^{36}Ar^{15}N^+$on $^{51}V^+$).

Elimination of hydrogen containing interferences through proton transfer reactions also takes place in the reaction cell (Tanner et al. 2002): $AH^+ + NH_3 \rightarrow NH_4^+ + A$ (e.g., $^{94}Zr^{17}O^1H^+$ on $^{112}Cd^+$, $^{38}ArH^+$ for $^{39}K^+$, $^{35}Cl^{16}OH^+$ for $^{52}Cr^+$). Condensation or clustering reactions with NH_3 or scattering can reduce the analyte signal, but this occurs at a lower rate. These reactions form new polyatomic species with the interfering ion (A^+) or the analyte ion (B^+) at a new m/z ratio (Olesik and Jones 2006): $B^+ + R \rightarrow BR_1^+ + R_2$ and $A^+ + R \rightarrow AR_1 + R_2$; $A^+ + NH_3 \rightarrow A.NH_3^+$, where R is the reaction gas and 1 and 2 are fragments. Some examples of condensation and clustering reactions with NH_3 gas are (Baranov and Tanner 1999; D'Ilio et al. 2011; Olesik and Jones 2006; Tanner et al. 2002): $V^+ + NH_3 \rightarrow VNH^+ + H_2$; $As^+ + NH_3 \rightarrow AsNH^+ + H_2$ or $As^+ + NH_3 \rightarrow AsNH_2^+ + H$; $Cl^+ + NH_3 \rightarrow NH_2Cl^+ + H$; $Ni^+ + NH_3 \rightarrow Ni^+.NH_3$; $V^+ + NH_3 \rightarrow V^+.NH_3$.

2.5.2 RPq Optimization

The reaction cell quadrupole band-pass was also adjusted by varying the rejection parameter q (RPq) to eject polyatomic reaction products arising from trace impurities in the cell gas. The optimal combination of the RPq value (0.40–0.80) and the NH_3 gas flow (0.25–0.80 $mLmin^{-1}$) given in Table 3 provided the maximum signal-to-noise ratio, which increased to 552–6,867 from only 1.6–58.9 in the standard mode for As, Zn, V, Ni, and Cd.

2.5.3 Quality Control/Assurance

Method detection limits (MDLs) were calculated by averaging 10 replicated analysis results of spiked standards in the matrix matched blank solution (6 mL HNO_3, 2 mL HCl, 1 mL HF, 8 mL 5 % H_3BO_3) performed both in standard and DRC mode of operation. The DRC mode reduced detection limits for V, Zn, and As significantly (47–91 %) compared with the standard mode as summarized in Table 3. Detection limit for As was decreased slightly from 2.7 to 2.5 $\mu g\ L^{-1}$ (only 5.4 % reduction) while no improvement was achieved for Ni probably because of high blank intensities at m/z 60 (Danadurai et al. 2011). Accuracy was characterized by comparing certified concentrations of elements in the reference materials with three separate measurements over the duration of this study. Recoveries of all elements measured in the DRC mode were between 88–112 % (Table 3). Performance measures including BECs, MDLs, and recoveries proved that the reaction cell allowed marked improvements in measurements of several anthropogenic metals including V, Ni, Zn, As, and Cd in road dusts similar to aerosols (Danadurai et al. 2011). DRC-q-ICP-MS analysis was performed using the optimized NH_3 flow rates and RPq values.

Elemental recoveries from three reference materials measured using the method described above are summarized in Table 4. BCR 723 and SRM 2556 contain only certified amounts of PGEs and therefore served to validate our measurements of Rh, Pd, and Pt. SRM 1648a was used to validate measurements of numerous other elements since it only contains certified values of non-PGEs. Average Rh, Pd and Pt recoveries from SRM 2556 were 107.8, 109.5 and 106.6 %, respectively, and those from BCR 723 were 101.6, 85.2 and 103.4 %. Non-PGEs, including rare earths (i.e. lanthanoids), were also recovered quantitatively recovered (85–115 %). These results demonstrate the accuracy of our ICP-MS and sample preparation protocols necessary for the accurate quantitation of numerous crustal and anthropogenic elements alongside PGEs necessary for source identification and apportionment.

3 Rh, Pd, and Pt Concentrations in Road/Tunnel Dust and Airborne PM

Table 5 summarizes PGE concentrations in tunnel dusts (n = 3), tunnel gutter (n = 1), and road dusts (n = 3) from this study along with the range and average values measured in soils, tunnel and road dusts in other parts of the world. Rh, Pd,

Table 4 Analysis of certified and indicative elements from three reference materials

Element	Atomic mass	BCR-723 (μg/g)		SRM 2556 (μg/g)		SRM 1684a (μg/g)	
		Supplied value	Measured value	Supplied value	Measured value	Supplied value	Measured value
Mg	24					**8,130 ± 120**	8,171 ± 323
Al	27	37,500 ± 2,200	37,307 ± 1,457	400,000	449,418 ± 34,840	**34,300 ± 1,300**	34,252 ± 2,883
Si	28					128,000 ± 4,000	124,531 ± 8,248
K	39					**10,560 ± 490**	10,387 ± 1,226
Ca	40					**58,400 ± 1900**	54,401 ± 5,665
Ti	48	2,580 ± 130	2,259 ± 45			**4,021 ± 86**	4,022 ± 250
V	51	75 ± 1.9	90 ± 2.3			**127 ± 11**	128 ± 8.6
Cr	52	440 ± 18	427 ± 47			**402 ± 13**	407 ± 20
Mn	55	1,280 ± 40	1,214 ± 21			**790 ± 44**	788 ± 35
Fe	56	32,900 ± 2,000	32,520 ± 921	8,000	8,705 ± 660	**39,200 ± 2,100**	37,552 ± 2,379
Ni	59	171 ± 3.0	167 ± 15			**81 ± 6.8**	80 ± 1.4
Co	59	30 ± 1.6	30 ± 0.42			**18 ± 0.68**	18 ± 0.71
Cu	64					**610 ± 70**	554 ± 34
Zn	65	1,660 ± 100	1,621 ± 80			**4,800 ± 270**	4,804 ± 457
As	75					**116 ± 3.9**	129 ± 16
Se	79					**27 ± 1.1**	22 ± 3.5
Rb	85	75 ± 5	70 ± 1.8			**51 ± 1.5**	45 ± 1.8
Sr	88	254 ± 19	241 ± 5.5			**215 ± 17**	207 ± 9.1
Y	89	13 ± 1.8	13 ± 0.52				

(continued)

Table 4 (continued)

Element	Atomic mass	BCR-723 (μg/g)		SRM 2556 (μg/g)		SRM 1684a (μg/g)	
		Supplied value	Measured value	Supplied value	Measured value	Supplied value	Measured value
Zr	91			300	317 ± 12		
Mo	96	40 ± 0.6	42 ± 2.4				
Rh	103	**0.0128 ± 0.0013**	0.0130 ± 0.0012	**51 ± 0.50**	55 ± 2.5		
Pd	106	**0.0061 ± 0.0019**	0.0052 ± 0.0014	**326 ± 1.6**	357 ± 22		
Cd	112	2.5 ± 0.4	2.6 ± 0.06			**74 ± 2.3**	74 ± 8.5
Sb	122	28 ± 2.3	26 ± 0.53			**45 ± 1.4**	45 ± 4.1
Cs	133					3.4 ± 0.20	3.0 ± 0.05
Ba	137	460 ± 40	477 ± 14	100	95 ± 13		
La	139			7,000	6,894 ± 206	39 ± 3.0	39 ± 5.2
Ce	140			10,000	11,094 ± 296	**55 ± 2.2**	52 ± 2.3
Sm	150					4.3 ± 0.30	4.5 ± 0.43
Hf	178	2.2 ± 0.7	2.0 ± 0.05				
W	184					4.6 ± 0.30	5.1 ± 1.1
Pt	195	**0.0813 ± 0.0025**	0.0841 ± 0.0058	**697 ± 2.3**	743 ± 89		
Pb	207	866 ± 16	928 ± 61	**6,228 ± 49**	6,635 ± 152	**6,550 ± 330**	6,178 ± 361
Th	232	4.8 ± 0.5	4.6 ± 0.26				

Notes Values in **bold font** correspond to certified values and those in regular font are only indicative (uncertified) values. Note that BCR 723 and SRM 2556 contain certified concentrations of Rh, Pd, and Pt whereas SRM 1648a only has certified concentrations of non-PGEs. Standard deviations for three separate digestions and ICP measurements are also provided

Table 5 Summary of PGEs abundances in road and tunnel dusts and soils from this and other studies

Location, sampling year	Sample type and remarks	Rh (ng/g)	Pd (ng/g)	Pt (ng/g)	Reference
Houston, TX (USA), 2012	Washburn Tunnel dust	152 ± 52.3 (116–212)	770 ± 208 (590–998)	529 ± 130 (409–668)	This study (Spada et al. 2012)
	Washburn Tunnel gutter	273	717	1079	
	Surface road dust	6.8 ± 1.3 (5.9–8.4)	53.5 ± 30.2 (33.3–88.2)	106 ± 21.5 (90.8–131)	
Prague, Ostrava (Czech Republic), 2006	Soil (0–10 cm)	<0.08–3.86	<0.45–49.8	<0.70–160	(Mihajevic et al. 2013)
	Soil (10–20 cm)	<0.08–2.36	<0.45–36.6	<0.70–77.8	
	Soil (20–30 cm)	<0.08–1.15	<0.45–23.5	<0.70–54.5	
China and India, 2007–2009	Road dust	0.1–134	0.1–538	0.4–385	(Pan et al. 2013)
Sheffield (UK)	Road dust	14–113	26–453	27–408	(Prichard et al. 2009)
China and India, 2004–2006	Soil	0.24–34.5	1.31–120	2.59–160	(Pan et al. 2009)
Ioannina (Greece)	Roadside soil	5.7–49.5	1.8–14.0	2.8–225	(Tsogas et al. 2009)
	Road dust	6.1–64.6	2.1–18.2	3.2–306	
Hawaii (USA), 2002	Road dust	5.18 ± 5.10 (0.24–15.8)	29.1 ± 32.4 (1.7–101)	51.8 ± 53.0 (4.1–174)	(Sutherland et al. 2008)
Germany, 1999 and 2004	Soil	20 (7–36)	83 (20–191)	132 (41–254)	(Zereini et al. 2007)
London (England), 2000	Road dust	22.4 ± 4.7	121 ± 12.0	15.9 ± 7.5	(Hooda et al. 2007)
	Roadside soil, 5 m-distance	3.5 ± 2.0	84.2 ± 10.9	2.0 ± 1.7	
Hawaii (USA), 1999–2000	Road dust	5.57 (0.36–20.1)	17.7 (2.1–105)	56.4 (4.44–293)	(Sutherland et al. 2007)
	Road dust	6.23 (0.48–64.1)	16.4 (3.37–70.3)	70.2 (8.54–506)	
	Soil	0.07 ± 0.014	1.12 ± 0.19	1.98 ± 0.63	
Beijing (China), 2002–2004	Road dust, 2002	22.7 (2.8–97.1)	34.2 (6.6–116)	15.9 (4.2–39.5)	(Wang et al. 2007)
	Road dust, 2004	79.7 (10.4–236)	19.9 (1.6–124)	97.2 (4.0–356)	

(continued)

Table 5 (continued)

Location, sampling year	Sample type and remarks	Rh (ng/g)	Pd (ng/g)	Pt (ng/g)	Reference
Braunschweig (Germany), 2005	Soil (0-2 cm)	0.18–10.7	0.89–43.3	1.3–50.4	(Wichmann et al. 2007)
	Soil (2-5 cm)	0.13–5.98	0.46–14.4	0.10–29.5	
	Soil (5-10 cm)	<BDL-1.68	0.41–3.80	0.10–8.80	
Sao Paulo (Brazil), 2002	Roadside soil	0.07–8.2	1.1–58.0	<BDL-17.4	(Morcelli et al. 2005)
Pert (Australia), 2002–2003	Road dust	42.0 (3.7–91.4)	184.5 (19.8–440)	206.7 (20.5–419.4)	(Whiteley 2005)
	Roadside soil	1.2–26.6	9.4–100.1	13.9–153.2	
Bialystok (Poland), 2000	Road dust	19.6	37.5	111	(Lesniewska et al. 2004)
	Tunnel dust	6.76	20.15	22.8	
Saarbrucken (Germany), 1999	Street dust	30–42	60–95	135–303	(Djingova et al. 2003b)
Pert (Australia)	Roadside soil	3.5–26.6	13.8–108	31.0–153	(Whiteley and Murray 2003)
	Road dust	8.8–91.4	58.1–440	53.8–419	
	Tunnel dust	22.5 ± 0.37	114 ± 23.3	142 ± 28.3	
Madrid (Spain)	Road dust	64	75	358	(Gomez et al. 2003)
	Road dust	44	26	171	
Graz (Austria), 1994 and 1998	Tanzenberg tunnel dust, CW-7	10.2	5.0	53.1	
	Tanzenberg tunnel dust, CW-8	12.9	5.4	81.9	

(continued)

Table 5 (continued)

Location, sampling year	Sample type and remarks	Rh (ng/g)	Pd (ng/g)	Pt (ng/g)	Reference
Goteborg (Sweden), 1998–2002	Road dust	101.8	70.8	325.5	(Gomez et al. 2002)
Rome (Italy), 1998–2002	Road dust	4.8	202.7	34.0	
Goteborg (Sweden)	Road dust	74	56	213	(Rauch et al. 2002)
Karlsruhe (Germany), 1999	Road dust	26	29	244	(Sures et al. 2002)
Mexico City (Mexico)	Roadside soil	0.2–39.1	1.1–101	1.1–333	(Morton et al. 2001)
Goteborg (Sweden), 1998	Road dust	91.3	81.0	195.3	(Motelica-Heino et al. 2001)
South Bend, IN (USA)	Roadside soil	0.16–6.7	2.1–31.8	5.2–73.2	(Ely et al. 2001)
Perth (Australia)	Highway soil	2.6–3.5	8.4–14.4	13.3–22.8	
London (England), 1995–1996	Soil and road dust	1–70	1–70	<10–500	(Jarvis et al. 2001)
Karlsruhe (Germany)	Road dust	18.7	21.3	101.3	(Sures et al. 2001)
Frankfurt (Germany), 1994–1995	Harber Tunnel dust	22	63	131	(Zereini et al. 2001b)
	Indoor Parking lot road dust	38	108	232	
	Theater tunnel dust	23	32	129	
Goteborg (Sweden), 1998	Road dust	74	56	189	(Rauch et al. 2000)
Rome (Italy), 1998–1999	Road dust	0.5–11.1	11.8–504	1.5–62.2	(Petrucci et al. 2000)
Graz (Austria), 1994, 1998	Tanzenberg tunnel dust, 1994	10.3 ± 1.4	4.0 ± 1.3	55 ± 8	(Schramel et al. 2000)
	Tanzenberg tunnel dust, 1998	12.8	5.5	81	
Styria (Austria), 1994	Tunnel dust	9.4 ± 0.8	17.4 ± 2.3	61.8 ± 1.5	(Kollensperger et al. 2000)

and Pt abundances in tunnel catwalk were 152 ± 52.3, 770 ± 208, and 529 ± 130 ngg^{-1}, respectively which are higher than those reported values for the Australian (Whiteley and Murray 2003) and European tunnels in Poland (Lesniewska et al. 2004), Austria (Gomez et al. 2003; Kollensperger et al. 2000; Schramel et al. 2000), and Germany (Zereini et al. 2001b). Rh and Pt were elevated in the tunnel gutter (273 ngg^{-1} for Rh and 1,079 ngg^{-1} for Pt) compared with Pd (717 ngg^{-1}), probably because of the regular washing of tunnel walls and catwalk which dissolved Pd given its higher water solubility and mobility (Jarvis et al. 2001). In Houston surface road dusts, Rh, Pd, and Pt abundances were between 5.9–8.4, 33.0–88.2, and 90.8–131 ngg^{-1}, respectively which are within the range of those reported values for the other road dusts through the world (Table 5). Variations reported in PGE concentrations in tunnel and road dusts are likely due to changing autocatalyst composition over time and differences in travel speeds, number of vehicles, vehicle types and engine models, type and age of catalyst, and fuel additives in different regions of the world.

PGE abundances in the tunnel and road dusts were 63 (Pd in the intersection of three major highways) to approx. 12,000 (Rh in tunnel dust) times higher than those reported in upper continental crust (UCC, Rh = 0.018, Pd = 0.526, and Pt = 0.599 ngg^{-1}) (Park et al. 2012). Several other elements including Cu, Zn, Ga, As, Mo, Cd, Sn, Sb, Ba, W, and Pb were also elevated in tunnel and road dusts with respect to UCC (Wedepohl 1995; Rudnick and Gao 2003), showing their anthropogenic nature. Higher concentrations of many vehicular elements in the tunnel on average than in surface roads (e.g. 2.4 fold for Zn to 22 fold for Rh) suggest that the Washburn Tunnel is largely isolated from ambient meteorology and dispersion.

PGE concentrations in airborne $PM_{2.5}$ and PM_{10} inside the tunnel and the ventilation air supply (collected in the fan room) are shown in Fig. 7. As shown earlier, PGE concentrations in the tunnel were substantially elevated relative to ambient air (Allen et al. 2001; Laschober et al. 2004; Limbeck et al. 2007).

Airborne particulate PGE concentrations measured in this study and reported elsewhere are summarized in Table 6. Average Rh, Pd, and Pt concentrations in ambient $PM_{2.5}$ collected in the ventilation air were 1.5, 11.1, and 4.5 pgm^{-3} respectively, which are in the range reported for other urban areas over the world (i.e., $0.3 \leq Rh \leq 4.2$, $0.7 \leq Pd \leq 27.4$, and $1.4 \leq Pt \leq 23.6$ pgm^{-3}) (Hays et al. 2011; Limbeck et al. 2007; Rauch et al. 2001; Zereini et al. 2012). Rh, Pd, and Pt concentrations approximately doubled in PM_{10} collected in the fan room compared with $PM_{2.5}$ averaging 3.8, 23.1, and 15.1 pgm^{-3} respectively. Again, these are within the range of PGE values for PM_{10} in urban areas given in Table 6 (i.e. $0.3 \leq Rh \leq 27.0$, $0.6 \leq Pd \leq 683$, and $0.6 \leq Pt \leq 80.9$ pgm^{-3}) (Gomez et al. 2002, 2003; Kanitsar et al. 2003; Limbeck et al. 2007; Petrucci et al. 2000; Rauch et al. 2001, 2005, 2006; Zereini et al. 2004, 2012).

Average Rh, Pd, and Pt concentrations increased 6.7–8.5 fold in $PM_{2.5}$ and 4.0–9.5 fold in PM_{10} inside the tunnel compared with the ambient (ventilation) air reaching 12.5, 91.1, and 30.1 pgm^{-3} in $PM_{2.5}$ and 36.3, 214, and 61.1 pgm^{-3} in PM_{10}, respectively. Higher PGE concentrations in PM_{10} compared with $PM_{2.5}$ in both ambient and tunnel air has also been reported earlier in Austria (Limbeck et al.

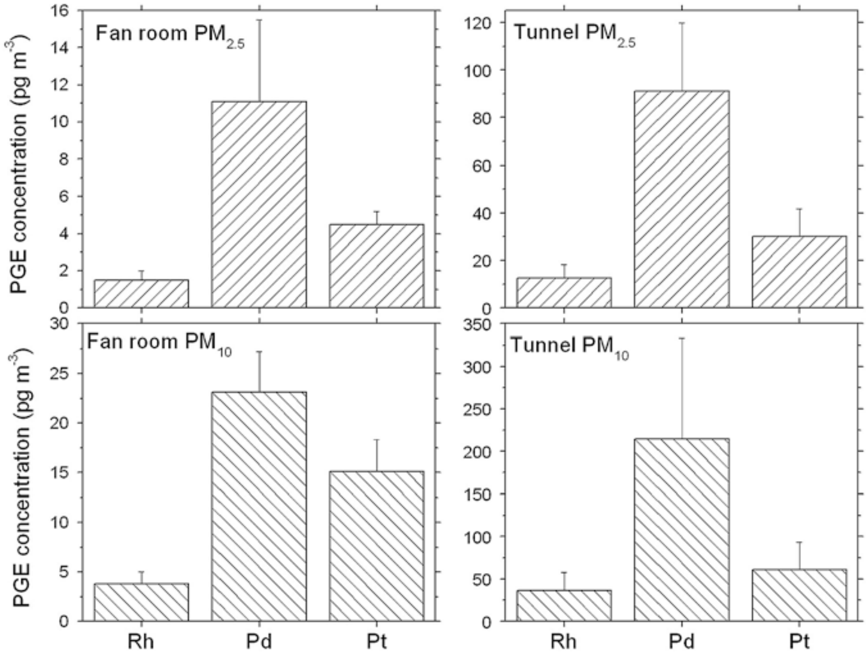

Fig. 7 PGE concentrations in airborne $PM_{2.5}$ and PM_{10} inside the Washburn Tunnel and ventilation (fan) room. Error bars represent 1 standard deviation from gravimetric mass measurements on 3 different days and 3 replicate PGE analyses

2007). Importantly, particulate PGE concentrations measured by us in the Washburn Tunnel are higher than those in European (Limbeck et al. 2007) and Mexican tunnels (Mancilla and Mendoza 2012) as summarized in Table 6.

Non-PGEs were also enriched in the tunnel compared with ambient air. One exception to this observation was La in $PM_{2.5}$, which is attributed to the proximity of petroleum refineries to the tunnel. The highest average ratio of concentration in the tunnel to that in the ventilation air for $PM_{2.5}$ was 9.0 for Rh and Cu. The same ratio varied from 1.8 (U) to 9.5 (Rh) for PM_{10}. On average, the 48 measured metals constituted 20.4 and 29.1 % of tunnel $PM_{2.5}$ and PM_{10} mass and 14.5 and 23.9 % of $PM_{2.5}$ and PM_{10} mass in the ventilation air, respectively. The metal fraction of PM mass was lower in the ambient environment than inside the tunnel, but similar to other reports in the Houston Ship Channel area (Bozlaker et al. 2013a; Kulkarni et al. 2006). Crustal elements (i.e. Mg, Al, Si, K, Ca, Ti, Mn, and Fe) accounted for nearly 96.5 % of measured elemental concentrations in PM_{10} compared with ~93 % in $PM_{2.5}$.

Enrichment factors for elements (X) were calculated with respect to Ti in the UCC (Park et al. 2012; Wedepohl 1995) using $EF_X = [X/Ti]_{Sample}/[X/Ti]_{UCC}$. The "natural" background in the ventilation air was subtracted from the corresponding tunnel PM concentrations (Grieshop et al. 2006; Handler et al. 2008; Laschober et al. 2004; Limbeck et al. 2007). La in $PM_{2.5}$ could not be subtracted due to the

Table 6 Rh, Pd, and Pt concentrations in airborne particulate matter in various locations around the world from this and other studies

Location and sampling year	Location	PM	Rh (pg/m^3)	Pd (pg/m^3)	Pt (pg/m^3)	Reference
Houston, TX (USA), 2012–2013	Ambient air	PM$_{2.5}$	1.5 ± 0.5 (1.1–1.8)	11.1 ± 4.4 (8.0–14.2)	4.5 ± 0.7 (4.0–5.0)	This study (Bozlaker et al. 2014)
	Washburn Tunnel	PM$_{2.5}$	12.5 ± 5.8 (8.5–16.6)	91.1 ± 28.6 (70.9-111)	30.1 ± 11.5 (22.0–38.2)	
	Ambient air	PM$_{10}$	3.8 ± 1.2 (3.0–4.7)	23.1 ± 4.1 (20.2–26.0)	15.1 ± 3.2 (12.9–17.4)	
	Washburn Tunnel	PM$_{10}$	36.3 ± 21.4 (21.2–51.5)	214 ± 119 (130–299)	61.1 ± 32.3 (38.2–84.0)	
Vienna (Austria)	Downtown, near-main road	TSP	NA	13.9 (5–29.1)	15.6 (7.5–26.8)	(Puls et al. 2012)
		PM$_{10}$	NA	10.6 (4.3–21.6)	9.9 (4.8–18.5)	
		PM$_{2.5}$	NA	4.9 (BDL-9.7)	2.3 (BDL-4.6)	
Monterrey (Mexico)	Loma Larga Tunnel	PM$_{2.5}$	NA	11.0–24.0	NA	(Mancilla and Mendoza 2012)
Frankfurt (Germany), 2008–2009	Urban	PM$_{10}$	3.2 (1.1–21.3)	43.9 (1.2–683)	12.4 (1.2–80.9)	(Zereini et al. 2012)
Deuselbach (Germany), 2008–2009	Rural	PM$_{10}$	1.2 (0.1–31.6)	2.1 (0.1–13.3)	2.0 (0.1–37.5)	
Neuglobsow (Germany), 2008–2009	Rural	PM$_{10}$	0.3 (0.1–3.6)	2.6 (0.2–10.9)	1.9 (0.1–19.3)	
Frankfurt (Germany), 2009–2010	Urban	PM$_{2.5}$	1.8 (0.7–4.2)	16.1 (5.4–27.4)	9.4 (2.6–23.6)	
Frankfurt (Germany), 2009–2010	Urban	PM$_{1.0}$	0.6 (0.2–1.9)	8.4 (2.6–31.4)	3.2 (0.9–10.5)	

(continued)

Table 6 (continued)

Location and sampling year	Location	PM	Rh (pg/m^3)	Pd (pg/m^3)	Pt (pg/m^3)	Reference
Raleigh, NC (USA)	Near highway	$PM_{10-2.5}$	0.4	1	3	(Hays et al. 2011)
		$PM_{2.5-0.1}$	1	10	10	
		$PM_{0.1}$	BDL	BDL	BDL	
Los Angeles, CA (USA)	Urban, rural, coastal, inland, near-freeway	PM $_{10–2.5}$	BDL	NA	BDL–10	(Pakbin et al. 2011)
Neuglobsow (Germany)	Background	PM_{10}	NA	0.3 (0.06–7.4)	NA	(Alsenz et al. 2009)
Deuselbach (Germany)	Background	PM_{10}	NA	0.6 (<0.05–9.7)	NA	
Frankfurt (Germany)	High traffic	PM_{10}	NA	20.7 (1.3–103)	NA	
Vienna (Austria), 2005	Kaisermuhlen Tunnel	TSP	NA	18 (10–33)	79 (54–144)	(Limbeck et al. 2007)
		PM_{10}	NA	8.8 (4.0–19)	30 (20–52)	
		$PM_{2.5}$	NA	4.9 (2.6–7.9)	12 (8.5–22)	
	Ambient	TSP	NA	3.1 (1.6–7.5)	24 (10–37)	
		PM_{10}	NA	2.0 (1.5–4.4)	13 (6.2–25)	
		$PM_{2.5}$	NA	1.7 (1.5–2.8)	6.5 (6.2–8.8)	

(continued)

Table 6 (continued)

Location and sampling year	Location	PM	Rh (pg/m^3)	Pd (pg/m^3)	Pt (pg/m^3)	Reference
Braunschweig (Germany), 1999	Urban	TSP	1.2	33.9	6	(Wichmann et al. 2007)
Braunschweig (Germany), 2005	Urban	TSP	10	37.8	159	
Buenos Aires (Argentina), 2001	Urban sites	PM_{10}	3.9 (0.3–16.8)	NA	12.9 (2.3–47.7)	(Bocca et al. 2006)
Mexico city (Mexico) 1991	Low to high traffic	PM_{10}	1.2	2.7	1.7	(Rauch et al. 2006)
Mexico city (Mexico) 2003		PM_{10}	2.8	10.2	9.6	
Mexico city (Mexico) 2003		PM_{10}	3.2	11	9.3	
Boston, MA (USA), 2002–2003	Urban	PM_{10}	1.3 (BDL-5.9)	7.1 (0.8–39)	6.2 (0.6–36)	(Rauch et al. 2005)
	Urban	PM_{10}	2.2 (BDL-5.9)	11 (1–26)	9.4 (0.62–17)	
Frankfurt (Germany), 2001–2002	High traffic	PM_{22}	4 (<0.1–12)	15 (<0.1–44)	23 (2–55)	(Zereini et al. 2005)
	Low traffic	PM_{22}	1 (<1–2)	6 (<1–39)	6 (1–17)	
	Background	PM_{22}	1 (<1–3)	3 (<1–11)	5 (1–27)	
Frankfurt am Main (Germany), 2001–2002	High traffic	PM_{22}	3.9 (<0.5–11.6)	14.7 (<0.6–44.3)	23.0 (2.4–55.4)	(Zereini et al. 2004)
	Low traffic	PM_{22}	0.9 (<0.5–2.2)	6.0 (<0.6–38.9)	6.0 (1.3–17.2)	
	Non-urban	PM_{22}	0.5 (<0.1–2.8)	2.8 (<0.5–11.2)	5.1 (0.4–26.6)	
	High traffic	PM_{10}	2.9 (1.8–4.5)	25.1 (9.4–29.3)	15.7 (8.7–28.4)	
	Low traffic	PM_{10}	0.7 (0.7–1.1)	8.9 (5.1–15.6)	6.2 (4.1–9.5)	
	Non-urban	PM_{10}	0.8 (0.3–1.5)	7.8 (4.7–11.7)	5.2 (3.0–7.9)	

(continued)

Table 6 (continued)

Location and sampling year	Location	PM	Rh (pg/m^3)	Pd (pg/m^3)	Pt (pg/m^3)	Reference
Madrid (Spain)	Urban highway	PM$_{10}$	27	5.1	15	(Gomez et al. 2003)
	Downtown	PM$_{10}$	9.1	32	19	
Vienna (Austria), 2002	High traffic	PM$_{10}$ TSP	0.4 (0.3–0.4) 6.6 (3.9–8.3)	2.6 (1.9–3.0) 14.4 (10.4–17.9)	4.3 (3.0–6.3) 38.1 (31.4–46.0)	(Kanitsar et al. 2003)
Madrid (Spain), 1998–2000	Urban, beltway, background sites	PM$_{10}$	4.2	BDL	15.6	(Gomez et al. 2002)
Goteborg (Sweden), 1998–2000		PM$_{10}$	3	4.1	12.3	
Sheffield (England), 1998–2000		PM$_{10}$	BDL	BDL	3.9	
London (England), 1998–2000		PM$_{10}$	BDL	BDL	5.6	
Rome (Italy), 1998–2000		PM$_{10}$	2.6	51.4	10.5	
Munich (Germany), 1998–2000		PM$_{10}$	0.3	BDL	4.1	
Goteborg (Sweden), 1999	Low traffic	PM$_{10}$	0.6 (0.3–1.2)	1.8 (< 0.6–4.4)	2.1 (0.9–3.0)	(Rauch et al. 2001)
	High traffic	PM$_{10}$	2.9 (1.3–4.3)	4.9 (1.3–9.7)	14.1 (7.6–19.2)	
	Low traffic	PM$_{2.5}$	0.5 (0.3–0.6)	1.4 (0.7–2.5)	2.7 (1.4–6.3)	
	High traffic	PM$_{2.5}$	1.6 (1.0–2.7)	1.5 (0.7–2.2)	5.4 (3.9–7.2)	

(continued)

Table 6 (continued)

Location and sampling year	Location	PM	Rh (pg/m^3)	Pd (pg/m^3)	Pt (pg/m^3)	Reference
Offenbach (Germany), 1988–1989		TSP	<0.2–1.0	NA	0.9–20.0	(Zereini et al. 2001a)
Frankfurt (Germany), 1992–1998		TSP	<0.5–15.0	NA	19.5–246	
Madrid (Spain)	High traffic	PM$_{10}$	BDL-9.3	NA	3–15.5	(Gomez et al. 2000)
Rome (Italy), 1998–1999	Rural, low traffic	PM$_{10}$	0.5 (<0.2–0.7)	4.6 (2.1–7.1)	0.5 (<0.5)	(Petrucci et al. 2000)
	Urban, high traffic	PM$_{10}$	2.3–5.4	21.5–78.2	9.4–37.1	

NA Not analyzed; *BDL* Below detection limit; *TSP* Total suspended particles very strong influence of nearby petroleum refineries (Kulkarni et al. 2006). In any case, subtracting ambient concentrations reduced enrichment factors for vehicular-related metals in both size modes by only 8.4 % on average. The biggest influences were for Pb in $PM_{2.5}$ and W in both size fractions which reduced by 47 % and approx. 65 %, respectively following subtraction.

Enrichment factors for traffic related elements in $PM_{2.5}$, PM_{10}, and dust material from the tunnel are given in Fig. 8 along with dusts from Houston surface roadways (n = 3). Inside the tunnel, most elements including Li, Be, Mg, Al, Si, K, Ti, V, Cr, Mn, Fe, Ni, Co, Rb, Sr, Y, Cs, Th, U, and lanthanoids had predominantly crustal origins with their EFs → 1. Both crustal and anthropogenic sources appear to have contributed to Ca, Zr, and W given their moderate EFs (3-10). Substantially higher EFs for Cu, Zn, Ga, As, Mo, Rh, Pd, Cd, Sn, Sb, Ba, Pt, and Pb (10–36,575) indicates their origins from light-duty vehicles in the tunnel. Of these elements, Rh, Pd, and Pt had the highest EFs (average 36,575, 9,142, and 2,549 for $PM_{2.5}$; 20,996, 4,250, and 890 for PM_{10}; 15,700, 2,726, and 1,642 for tunnel dust, respectively) providing strong evidence for their release from light-duty vehicles. The enrichment of Cu, Ba, Zr, Zn, Sb, Sn, and Mo inside the tunnel is attributed to tire wear and brake lining abrasion (Adachi and Tainosho 2004; Bukowiecki et al. 2010; Garg et al. 2000; Hildeman et al. 1991; Hjortenkrans et al. 2007; Thorpe and Harrison 2008). Zn, Cd, Cu, and Pb (Cadle et al. 1999; Saint'Pierre et al. 2004; Sternbeck et al. 2002) are emitted via the tailpipe; Ga and W are employed in vehicle electronics (Grieshop et al. 2006; Spada et al. 2012); and Zr, Ba, W, and PGEs are emitted from deteriorating washcoats (Ravindra et al. 2004; Zereini and Alt 2000). Cu, Zr, Rh, Pd, Sb, and Pt appear to be unique markers of gasoline-driven vehicles since they were enriched to a significantly greater extent in the tunnel compared with the ventilation air.

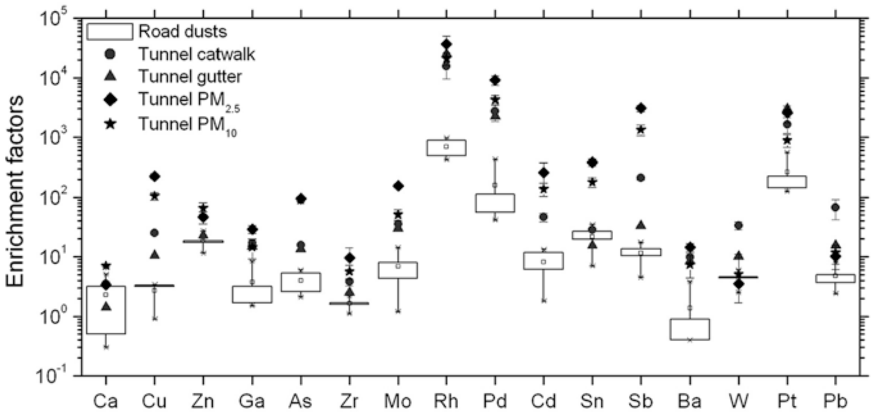

Fig. 8 Enrichment factors for traffic related elements enriched in $PM_{2.5}$, PM_{10}, and tunnel dust. Dusts from four surface roadways in Houston are also depicted

Pd/Pt ratios in the tunnel ranged between 1.5 and 3.5, whereas it has been reported to be < 1 in Europe (Limbeck et al. 2007; Rauch et al. 2001; Schafer et al. 1999) and in North Carolina (Hays et al. 2011). This is attributed to changes in vehicle fleet characteristics with location and varying PGE concentrations embedded in catalytic converters for different vehicle models.

3.1 PGE Characterization

Simultaneous variations in Rh, Pd, and Pt concentrations in road/tunnel dusts (Fig. 9) and airborne $PM_{2.5}$ and PM_{10} (Fig. 10) measured in this study are superposed on several other PGE bearing matrices by normalizing their concentrations so

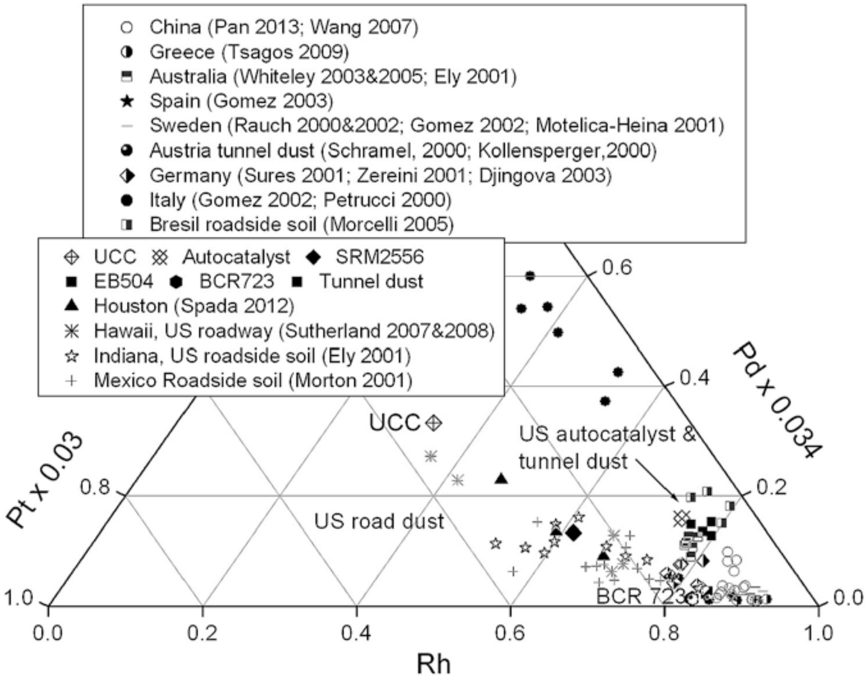

Fig. 9 Rh, Pd, Pt ternary diagram for various tunnel and road dusts normalized so that average UCC concentrations appear at the centroid. Tunnel/road dusts collected in this study are depicted alongside a mixed-lot random sample of several U.S. autocatalytic converters, SRM 2556 (a 1993 used autocatalyst material from NIST), European spent autocatalyst (ERM-EB504), Austrian tunnel dust (BCR-273), and other road/tunnel dusts from the literature (Djingova et al. 2003b; Ely et al. 2001; Gomez et al. 2002, 2003; Kollensperger et al. 2000; Morcelli et al. 2005; Morton et al. 2001; Motelica-Heino et al. 2001; Pan et al. 2013; Petrucci et al. 2000; Rauch et al. 2000, 2002; Schramel et al. 2000; Sures et al. 2001; Sutherland et al. 2007, 2008; Tsogas et al. 2009; Wang et al. 2007; Whiteley 2005; Whiteley and Murray 2003; Zereini et al. 2001b)

that average UCC abundances (Park et al. 2012) appear at the centroid. Such ternary plots are increasingly being employed to better visualize differences in particulate matter characteristics e.g. (Bozlaker et al. 2013a; Moreno et al. 2008; Bozlaker et al. 2013b; Moreno et al. 2010).

Tunnel/road dust and airborne $PM_{2.5}$ and PM_{10} from the Washburn Tunnel and ambient air (Bozlaker et al. 2014; Spada et al. 2012) as well as PM_{10} from Boston, MA (Rauch et al. 2005) in Figs. 9 and 10 was depleted in Pt and Pd but enriched in Rh shifting them away from the UCC centroid towards the Rh apex (lower right hand corner). Importantly, these environmental samples locate very close to the mixed-lot recycled United States autocatalytic converters sample supplied by Engelhard Corp (see Sect. 2.2.3). This provides strong evidence that the principal PGE source inside the tunnel is freshly-emitted autocatalyst from light-duty vehicles. Houston area surface road dusts were significantly altered compared to newly-released airborne PGE particles as they had higher Pt concentrations compared with Pd and Rh. This is due to weathering in the ambient environment wherein Pd and Rh dissolve more readily in water and consequently are more mobile in the environment (Jarvis et al. 2001). Houston road dusts showed similar PGE distribution

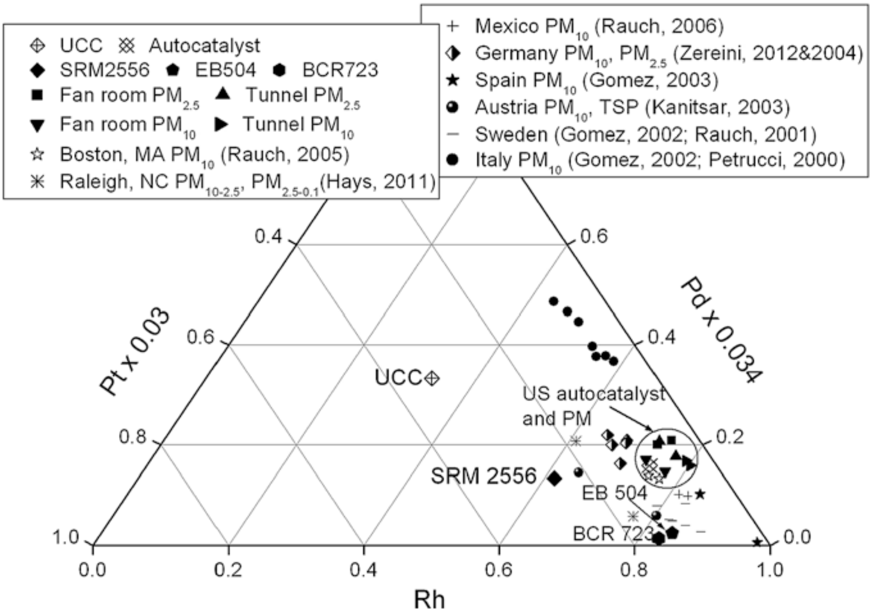

Fig. 10 Rh, Pd, Pt ternary diagram for various aerosols normalized so that average UCC concentrations appear at the centroid. Airborne $PM_{2.5}$ and PM_{10} collected in this study are depicted alongside a mixed-lot random sample of several U.S. autocatalysts, SRM 2556 (a 1993 used autocatalyst material from NIST), European spent autocatalyst (ERM-EB504), Austrian tunnel dust (BCR-273), and other airborne PM data from the literature (Gomez et al. 2002, Gomez et al. 2003; Hays et al. 2011; Kanitsar et al. 2003; Petrucci et al. 2000; Rauch et al. 2001, 2005, 2006; Zereini et al. 2004, 2012)

patterns to other soil and road dust samples from the United States (Ely et al. 2001; Sutherland et al. 2007, 2008) and Mexico (Morton et al. 2001). Road/tunnel dust and airborne PM samples from the Washburn Tunnel were spatially separated from an older used autocatalyst (SRM-2556), European tunnel dust (BCR 723), European autocatalysts (EB-504), as well as Chinese (Pan et al. 2013; Wang et al. 2007), European (Djingova et al. 2003b; Gomez et al. 2002, 2003; Kanitsar et al. 2003; Kollensperger et al. 2000; Motelica-Heino et al. 2001; Petrucci et al. 2000; Rauch et al. 2000, 2001, 2002: Schramel et al. 2000; Sures et al. 2001; Tsogas et al. 2009; Zereini et al. 2001b, 2004, 2012), Australian (Ely et al. 2001; Whiteley 2005; Whiteley and Murray 2003), and Mexican (Rauch et al. 2006) road dusts and airborne PM. These differences are attributed to changes in the relative PGE composition of autocatalysts over time as well as geographical differences in vehicle fleets, driving habits, traffic speed and density, environmental regulations, and environmental transport and fate of PGEs.

4 Concluding Remarks

New sample preparation and corresponding ICP-MS methods were developed to comprehensively characterize the composition of road dusts and airborne PM in terms of three Pd-group PGEs (viz. Rh, Pd, and Pt) along with lanthanoids, transition and representative elements. This analytical technique overcomes challenges arising from the use of HCl and HNO_3 required for quantitative PGE extraction, which often cause isobaric interferences and spectral overlaps during ICP-MS analysis. This was accomplished by using a cation-exchange column during sample preparation to reduce concentrations of many PGE interferents. We measured the detailed elemental composition of several surface road dusts and dusts from an underwater tunnel as well as PM in the tunnel ventilation air and the air inside the tunnel in the fourth largest city in the United States (i.e. Houston, Texas). Our measurements show that Cu, Zr, Rh, Pd, Sb, and Pt are unique elemental tracers of PM derived from predominantly gasoline-driven light-duty vehicles. These results highlight the need to quantify PGE emissions in order to more accurately quantify the contributions of light-duty vehicles to airborne PM in urban environments. One potential shortcoming of our work is that we collected samples integrated over 3–4 weeks in order to obtain sufficient PM mass to quantify most elements above ICP-MS detection limits. Potentially, the use of magnetic sector field instruments might allow better elemental detection thereby allowing greater time resolution during sampling. Additionally, our tunnel sampling only covered the months of November and December. Longer term sampling is necessary to include potential effects of seasonal variations in ambient temperature and weather conditions to comprehensively establish PGE emissions. Further, more efforts are necessary to measure PGEs in ambient air near highways and residential areas to better understand the source contributions and human exposure especially in the United States, where such data are sorely lacking. We intend to undertake such a sampling campaign in the near future.

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References

Adachi K, Tainosho Y (2004) Characterization of heavy metal particles embedded in tire dust. Environ Int 30(8):1009–1017

Allen JO, Mayo PR, Hughes LS, Salmon LG, Cass GR (2001) Emissions of size-segregated aerosols from on-road vehicles in the Caldecott Tunnel. Environ Sci Technol 35 (21):4189–4197

Alsenz H, Zereini F, Wiseman CLS, Püttmann W (2009) Analysis of palladium concentrations in airborne particulate matter with reductive co-precipitation, He collision gas, and ID-ICP-Q-MS. Anal Bioanal Chem 395(6):1919–1927

Baranov VI, Tanner SD (1999) A dynamic reaction cell for inductively coupled plasma mass spectrometry (ICP-DRC-MS)—Part 1. The rf-field energy contribution in thermodynamics of ion-molecule reactions. J Anal At Spectrom 14(8):1133–1142

Bocca B, Caimi S, Smichowski P, Gomez D, Caroli S (2006) Monitoring Pt and Rh in urban aerosols from Buenos Aires, Argentina. Sci Total Environ 358(1–3):255–264

Bozlaker A, Buzcu-Guven B, Fraser MP, Chellam S (2013a) Insights into PM_{10} sources in Houston, Texas: Role of petroleum refineries in enriching lanthanoid metals during episodic emission events. Atmos Environ 69:109–117

Bozlaker A, Prospero JM, Fraser MP, Chellam S (2013b) Quantifying the contribution of long-range saharan dust transport on particulate matter concentrations in Houston, Texas, using Detailed Elemental Analysis. Environ Sci Technol 47:10179–10187

Bozlaker A, Spada NJ, Fraser MP, Chellam S (2014) Elemental characterization of $PM_{2.5}$ and PM_{10} emitted from light duty vehicles in the Washburn Tunnel of Houston, Texas: release of rhodium, palladium, and platinum. Environ Sci Technol. doi:10.1021/es4031003

Bukowiecki N, Lienemann P, Hill M, Furger M, Richard A, Amato F, Prevot ASH, Baltensperger U, Buchmann B, Gehrig R (2010) PM10 emission factors for non-exhaust particles generated by road traffic in an urban street canyon and along a freeway in Switzerland. Atmos Environ 44 (19):2330–2340

Cadle SH, Mulawa PA, Hunsanger EC, Nelson K, Ragazzi RA, Barrett R, Gallagher GL, Lawson DR, Knapp KT, Snow R (1999) Composition of light-duty motor vehicle exhaust particulate matter in the Denver, Colorado area. Environ Sci Technol 33(14):2328–2339

Cairns WRL, De Boni A, Cozzi G, Asti M, Borla EM, Parussa F, Moretto E, Cescon P, Boutron C, Gabrieli J, Barbante C (2011) The use of cation exchange matrix separation coupled with ICP-MS to directly determine platinum group element (PGE) and other trace element emissions from passenger cars equipped with diesel particulate filters (DPF). Anal Bioanal Chem 399 (8):2731–2740

D'Ilio S, Violante N, Majorani C, Petrucci F (2011) Dynamic reaction cell ICP-MS for determination of total As, Cr, Se and V in complex matrices: Still a challenge? A review. Analytica Chimica Acta 698(1–2):6–13

Chellam S, Kulkarni P, Fraser MP (2005) Emissions of Organic Compounds and Trace Metals in Fine Particulate Matter from Motor Vehicles: A Tunnel Study in Houston, Texas. J Air & Waste Mgmt Assoc 55(1):60–72

Danadurai KSK, Chellam S, Lee CT, Fraser MP (2011) Trace elemental analysis of airborne particulate matter using dynamic reaction cell inductively coupled plasma—mass spectrometry: application to monitoring episodic industrial emission events. Anal Chim Acta 686(1–2):40–49

Djingova R, Heidenreich H, Kovacheva P, Markert B (2003a) On the determination of platinum group elements in environmental materials by inductively coupled plasma mass spectrometry and microwave digestion. Anal Chim Acta 489(2):245–251

Djingova R, Kovacheva P, Wagner G, Markert B (2003b) Distribution of platinum group elements and other traffic related elements among different plants along some highways in Germany. Sci Total Environ 308(1–3):235–246

Dubiella-Jackowska A, Polkowska Z, Namiesnik J (2007) Platinum group elements: a challenge for environmental analytics. Polish J Environ Stud 16(3):329–345

Ely JC, Neal CR, Kulpa CF, Schneegurt MA, Seidler JA, Jain JC (2001) Implications of platinum-group element accumulation along U.S. roads from catalytic-converter attrition. Environ Sci Technol 35(19):3816–3822

Ely JC, Neal CR, O'Neill JA, Jain JC (1999) Quantifying the platinum group elements (PGEs) and gold in geological samples using cation exchange pretreatment and ultrasonic nebulization inductively coupled plasma-mass spectrometry (USN-ICP-MS). Chem Geol 157(3–4):219–234

Fang J, Jiang Y, Yan XP, Ni ZM (2005) Selective quantification of trace palladium in road dusts and roadside soils by displacement solid-phase extraction online coupled with electrothermal atomic absorption spectrometry. Environ Sci Technol 39(1):288–292

FHWA (2013) http://www.fhwa.dot.gov/policyinformation/travel_monitoring/tvt.cfm. Accessed 18 Nov 2013

Garg BD, Cadle SH, Mulawa PA, Groblicki PJ, Laroo C, Parr GA (2000) Brake wear particulate matter emissions. Environ Sci Technol 34(21):4463–4469

Gomez B, Gomez M, Sanchez JL, Fernandez R, Palacios MA (2001) Platinum and rhodium distribution in airborne particulate matter and road dust. Sci Total Environ 269(1–3):131–144

Gomez B, Palacios MA, Gomez M, Sanchez JL, Morrison G, Rauch S, McLeod C, Ma R, Caroli S, Alimonti A, Petrucci F, Bocca B, Schramel P, Zischka M, Petterson C, Wass U (2002) Levels and risk assessment for humans and ecosystems of platinum-group elements in the airborne particles and road dust of some European cities. Sci Total Environ 299(1–3):1–19

Gomez MB, Gomez MM, Palacios MA (2000) Control of interferences in the determination of Pt, Pd and Rh in airborne particulate matter by inductively coupled plasma mass spectrometry. Anal Chim Acta 404(2):285–294

Gomez MB, Gomez MM, Palacios MA (2003) ICP-MS determination of Pt, Pd and Rh in airborne and road dust after tellurium coprecipitation. J Anal At Spectrom 18(1):80–83

Grieshop AP, Lipsky EM, Pekney NJ, Takahama S, Robinson AL (2006) Fine particle emission factors from vehicles in a highway tunnel: effects of fleet composition and season. Atmos Environ 40(2):S287–S298

Handler M, Puls C, Zbiral J, Marr I, Puxbaum H, Limbeck A (2008) Size and composition of particulate emissions from motor vehicles in the Kaisermuhlen-Tunnel, Vienna. Atmos Environ 42(9):2173–2186

Hays MD, Cho SH, Baldauf R, Schauer JJ, Shaferd M (2011) Particle size distributions of metal and non-metal elements in an urban near-highway environment. Atmos Environ 45(4):925–934

Hildeman LM, Markowski GR, Cass GR (1991) Chemical composition of emissions from urban sources of fine organic aerosol. Environ Sci Technol 25(4):744–759

Hjortenkrans DST, Bergback BG, Haggerud AV (2007) Metal emissions from brake linings and tires: case studies of Stockholm, Sweden 1995/1998 and 2005. Environ Sci Technol 41 (15):5224–5230

Hooda PS, Miller A, Edwards AC (2007) The distribution of automobile catalysts-cast platinum, palladium and rhodium in soils adjacent to roads and their uptake by grass. Sci Total Environ 384(1–3):384–392

Jarvis KE, Parry SJ, Piper JM (2001) Temporal and spatial studies of autocatalyst-derived platinum, rhodium, and palladium and selected vehicle derived trace elements in the environment. Environ Sci Technol 35(6):1031–1036

Kanitsar K, Koellensperger G, Hann S, Limbeck A, Puxbaum H, Stingeder G (2003) Determination of Pt, Pd and Rh by inductively coupled plasma sector field mass spectrometry (ICP-SFMS) in size-classified urban aerosol samples. J Anal At Spectrom 18(3):239–246

Kingston HM, Haswell SJ (eds) (1997) Microwave enhanced chemistry: Fundamentals, sample preparation, and applications. American Chemical Society, ACS Professional Reference Book Series, Washington

Kollensperger G, Hann S, Stingeder G (2000) Determination of Rh, Pd and Pt in environmental silica containing matrices: capabilities and limitations of ICP-SFMS. J Anal At Spectrom 15 (12):1553–1557

Kovacheva P, Djingova R (2002) Ion-exchange method for separation and concentration of platinum and palladium for analysis of environmental samples by inductively coupled plasma atomic emission spectrometry. Anal Chim Acta 464(1):7–13

Kulkarni P, Chellam S, Flanagan JB, Jayanty RKM (2007a) Microwave digestion—ICP-MS for elemental analysis in ambient airborne fine particulate matter: rare earth elements and validation using a filter borne fine particle certified reference material. Anal Chim Acta 599(2):170–176

Kulkarni P, Chellam S, Fraser MP (2006) Lanthanum and lanthanides in atmospheric fine particles and their apportionment to refinery and petrochemical operations in Houston, TX. Atmos Environ 40(3):508–520

Kulkarni P, Chellam S, Fraser MP (2007b) Tracking petroleum refinery emission events using lanthanum and lanthanides as elemental markers for $PM_{2.5}$. Environ Sci Technol 41 (19):6748–6754

Kulkarni P, Chellam S, Mittlefehldt DW (2007c) Microwave-assisted extraction of rare earth elements from petroleum refining catalysts and ambient fine aerosols prior to inductively coupled plasma-mass spectrometry. Anal Chim Acta 581(2):247–259

Laschober C, Limbeck A, Rendl J, Puxbaum H (2004) Particulate emissions from on-road vehicles in the Kaiserm.uhlen-tunnel (Vienna, Austria). Atmos Environ 38(14):2187–2195

Lesniewska BA, Godewska-Zylkiewicz B, Bocca B, Caimi S, Caroli S, Hulanicki A (2004) Platinum, palladium and rhodium content in road dust, tunnel dust and common grass in Bialystok area (Poland): a pilot study. Sci Total Environ 321(1–3):93–104

Lesniewska BA, Godlewska-Zylkiewicz B, Ruszczynska A, Bulska E, Hulanicki A (2006) Elimination of interferences in determination of platinum and palladium in environmental samples by inductively coupled plasma mass spectrometry. Anal Chim Acta 564(2):236–242

Limbeck A, Puls C, Handler M (2007) Platinum and palladium emissions from on-road vehicles in the Kaisermuhlen Tunnel (Vienna, Austria). Environ Sci Technol 41(14):4938–4945

Lough GC, Schauer JJ, Park JS, Shafer MM, Deminter JT, Weinstein JP (2005) Emissions of metals associated with motor vehicle roadways. Environ Sci Technol 39(3):826–836

Mancilla Y, Mendoza A (2012) A tunnel study to characterize $PM_{2.5}$ emissions from gasoline-powered vehicles in Monterrey, Mexico. Atmos Environ 59:449–460

Matusiewicz H, Lesinski M (2002) Electrodeposition sample introduction for ultra trace determinations of platinum group elements (Pt, Pd, Rh, Ru) in road dust by electrothermal atomic absorption spectrometry. Int J Environ Anal Chem 82(4):207–223

Mihajevic M, Galuskova I, Strnad L, Majer V (2013) Distribution of platinum group elements in urban soils, comparison of historically different large cities Prague and Ostrava, Czech Republic. J Geochem Explor 124:212–217

Moldovan M, Gomez MM, Palacios MA (1999) Determination of platinum, rhodium and palladium in car exhaust fumes. J Anal At Spectrom 44(8):1163–1169

Morcelli CPR, Figueiredo AMG, Sarkis JES, Enzweiler J, Kakazu M, Sigolo JB (2005) PGEs and other traffic-related elements in roadside soils from Sao Paulo, Brazil. Sci Total Environ 345 (1–3):81–91

Moreno T, Querol X, Alastuey A, de la Rosa J, de la Campa AMS, Minguillon M, Pandolfi M, Gonzalez-Castanedo Y, Monfort E, Gibbons W (2010) Variations in vanadium, nickel and lanthanoid element concentrations in urban air. Sci Total Environ 408(20):4569–4579

Moreno T, Querol X, Alastuey A, Pey J, Minguillon MC, Perez N, Bernabe RM, Blanco S, Cardenas B, Gibbons W (2008) Lanthanoid geochemistry of urban atmospheric particulate matter. Environ Sci Technol 42(17):6502–6507

Morton O, Puchelt H, Hernandez E, Lounejeva E (2001) Traffic-related platinum group elements (PGE) in soils from Mexico City. J Geochem Explor 72(3):223–227

Motelica-Heino M, Rauch S, Morrison GM, Donard OFX (2001) Determination of palladium, platinum and rhodium concentrations in urban road sediments by laser ablation-ICP-MS. Anal Chim Acta 436(2):233–244

Mukai H, Ambe Y, Morita M (1990) Flow injection inductively coupled plasma mass spectrometry for the determination of platinum in airborne particulate matter. J Anal At Spectrom 5(1):75–80

Olesik JW, Jones DR (2006) Strategies to develop methods using ion-molecule reactions in a quadrupole reaction cell to overcome spectral overlaps in inductively coupled plasma mass spectrometry. J Anal At Spectrom 21(2):141–159

Pakbin P, Ning Z, Shafer MM, Schauer JJ, Sioutas C (2011) Seasonal and spatial coarse particle elemental concentrations in the Los Angeles area. Aerosol Sci Technol 45(8):949–963

Pan S, Zhang G, Sun Y, Chakrabort P (2009) Accumulating characteristics of platinum group elements (PGE) in urban environments. China. Science of the Total Environment 407 (14):4248–4252

Pan SH, Sun YL, Zhang G, Chakraborty P (2013) Spatial distributions and characteristics of platinum group elements (PGEs) in urban dusts from China and India. J Geochem Explor 128:153–157

Park JW, Hu ZC, Gao S, Campbell IH, Gong HJ (2012) Platinum group element abundances in the upper continental crust revisited: New constraints from analyses of Chinese loess. Geochim Cosmochim Acta 93:63–76

Petrucci F, Bocca B, Alimonti A, Caroli S (2000) Determination of Pd, Pt and Rh in airborne particulate and road dust by high-resolution ICP-MS: a preliminary investigation of the emission from automotive catalysts in the urban area of Rome. J Anal At Spectrom 15(5):525–528

Prichard HM, Fisher PC (2012) Identification of platinum and palladium particles emitted from vehicles and dispersed into the surface environment. Environ Sci Technol 46(6):3149–3154

Prichard HM, Sampson J, Jackson M (2009) A further discussion of the factors controlling the distribution of Pt, Pd, Rh and Au in road dust, gullies, road sweeper and gully flusher sediment in the city of Sheffield. UK. Science of the Total Environment 407(5):1715–1725

Puls C, Limbeck A, Hann S (2012) Bioaccessibility of palladium and platinum in urban aerosol particulates. Atmos Environ 55:213–219

Rauch S, Hemond HF, Peucker-Ehrenbrink B, Ek KH, Morrison GM (2005) Platinum group element concentrations and osmium isotopic composition in urban airborne particles from Boston. Massachusetts. Environmental Science and Technology 39(24):9464–9470

Rauch S, Lu M, Morrison GM (2001) Heterogeneity of platinum group metals in airborne particles. Environ Sci Technol 35(3):595–599

Rauch S, Morrison GM, Moldovan M (2002) Scanning laser ablation-ICP-MS tracking of platinum group elements in urban particles. Sci Total Environ 286(1–3):243–251

Rauch S, Morrison GM, Motelica-Heino M, Donard OFX, Muris M (2000) Elemental association and fingerprinting of traffic related metals in road sediments. Environ Sci Technol 34 (15):3119–3123

Rauch S, Peucker-Ehrenbrink B, Molina LT, Molina MJ, Ramos R, Hemond HF (2006) Platinum group elements in airborne particles in Mexico City. Environ Sci Technol 40(24):7554–7560

Ravindra K, Bencs L, Van Grieken R (2004) Platinum group elements in the environment and their health risk. Sci Total Environ 318(1–3):1–43

Rudnick RL, Gao S (2003) Composition of the Continental Crust. In: Holland HD, Turekian KK (eds) Treatise on Geochemistry, vol 3. Pergamon/Elsevier, Boston, MA, pp 1-64. doi:10.1016/B0-08-043751-6/03016-4

Saint'Pierre TD, Dias LF, Maia SM, Curtius AJ (2004) Determination of Cd, Cu, Fe, Pb and Tl in gasoline as emulsion by electrothermal vaporization inductively coupled plasma mass spectrometry with analyte addition and isotope dilution calibration techniques. Spectrochimica Acta Part B-Atomic Spectroscopy 59(4):551–558

Schafer J, Eckhardt JD, Berner ZA, Stuben D (1999) Time-dependent increase of traffic-emitted platinum-group elements (PGE) in different environmental compartments. Environ Sci Technol 33(18):3166–3170

Schramel P, Zischka M, Muntau H, Stojanik B, Dams R, Gomez GM, Quevauviller P (2000) Collaborative evaluation of the analytical state-of-the-art of platinum, palladium and rhodium determinations in road dust. J Environ Monit 2(5):443–446

Simitchiev K, Stefanova V, Kmetov V, Andreev G, Sanchez A, Canals A (2008) Investigation of ICP-MS spectral interferences in the determination of Rh, Pd and Pt in road dust: Assessment of correction algorithms via uncertainty budget analysis and interference alleviation by preliminary acid leaching. Talanta 77(2):889–896

Simpson LA, Thomsen M, Alloway BJ, Parker A (2001) A dynamic reaction cell (DRC) solution to oxide-based interferences in inductively coupled plasma mass spectrometry (ICP-MS) analysis of the noble metals. J Anal At Spectrom 16(12):1375–1380

Spada N, Bozlaker A, Chellam S (2012) Multi-elemental characterization of tunnel and road dusts in Houston, Texas using dynamic reaction cell-quadrupole-inductively coupled plasma-mass spectrometry: Evidence for the release of platinum group and anthropogenic metals from motor vehicles. Anal Chim Acta 735:1–8

Sternbeck J, Sjodin A, Andreasson K (2002) Metal emissions from road traffic and the influence of resuspension - results from two tunnel studies. Atmos Environ 36(30):4735–4744

Sures B, Zimmermann S, Messerschmidt J, Von Bohlen A (2002) Relevance and analysis of traffic related platinum group metals (Pt, Pd, Rh) in the aquatic biosphere, with emphasis on palladium. Ecotoxicology 11(5):385–392

Sures B, Zimmermann S, Messerschmidt J, von Bohlen A, Alt F (2001) First report on the uptake of automobile catalyst emitted palladium by European eels (Anguilla anguilla) following experimental exposure to road dust. Environ Pollut 113(3):341–345

Sutherland RA, Pearson DG, Ottley CJ (2007) Platinum-group elements (Ir, Pd, Pt and Rh) in road-deposited sediments in two urban watersheds. Hawaii. Applied Geochemistry 22 (7):1485–1501

Sutherland RA, Pearson DG, Ottley CJ (2008) Grain size partitioning of platinum-group elements in road-deposited sediments: Implications for anthropogenic flux estimates from autocatalysts. Environ Pollut 151(3):503–515

Tanner SD, Baranov VI, Bandura DR (2002) Reaction cells and collision cells for ICP-MS: a tutorial review. Spectrochimica Acta Part B 57(9):1361–1452

Tanner SD, Baranov VI, Vollkopf U (2000) A dynamic reaction cell for inductively coupled plasma mass spectrometry (ICP-DRC-MS) - Part III. Optimization and analytical performance. J Anal At Spectrom 15(9):1261–1269

Thorpe A, Harrison RM (2008) Sources and properties of non-exhaust particulate matter from road traffic: a review. Sci Total Environ 400(1–3):270–282

Tsogas GZ, Giokas DL, Vlessidis AG, Aloupi M, Angelidis MO (2009) Survay of the distribution and time-dependent increase of platinum-group element accumulation along urban roads in Ioannina (NW Greece). Water Air Soil Pollut 201:265–281

Wang J, Zhu RH, Shi YZ (2007) Distribution of platinum group elements in road dust in the Beijing metropolitan area, China. J Environmental Sciences 19(1):29–34

Wedepohl KH (1995) The composition of the continental crust. Geochim Cosmochim Acta 59 (7):1217–1232

Whiteley JD (2005) Seasonal variability of platinum, palladium and rhodium (PGE) levels in road dusts and roadside soils, perth, Western Australia. Water Air Soil Pollut 160(1–4):77–93

Whiteley JD, Murray F (2003) Anthropogenic platinum group element (Pt, Pd and Rh) concentrations in road dusts and roadside soils from Perth, Western Australia. Sci Total Environ 317(1–3):121–135

Wichmann H, Anquandah GAK, Schmidt C, Zachmann D, Bahadir MA (2007) Increase of platinum group element concentrations in soils and airborne dust in an urban area in Germany. Sci Total Environ 388(1–3):121–127

Wiseman CLS, Zereini F (2009) Airborne particulate matter, platinum group elements and human health: a review of recent evidence. Sci Total Environ 407(8):2493–2500

Zereini F, Alsenz H, Wiseman CLS, Puttmann W, Reimer E, Schleyer R, Bieber E, Wallasch M (2012) Platinum group elements (Pt, Pd, Rh) in airborne particulate matter in rural vs. urban areas of Germany: concentrations and spatial patterns of distribution. Sci Total Environ 416:261–268

Zereini F, Alt F (eds) (2000) Anthropogenic platinum-group element emissions: their impact on man and environment. Springer, Berlin. doi:10.1007/978-3-642-59678-0

Zereini F, Alt F, Messerschmidt J, Von Bohlen A, Liebl K, Puttmann W (2004) Concentration and distribution of platinum group elements (Pt, Pd, Rh) in airborne particulate matter in Frankfurt am Main, Germany. Environ Sci Technol 38(6):1686–1692

Zereini F, Alt F, Messerschmidt J, Wiseman C, Feldmann I, Von Bohlen A, Muller J, Liebl K, Puttmann W (2005) Concentration and distribution of heavy metals in urban airborne particulate matter in Frankfurt am main, Germany. Environ Sci Technol 39(9):2983–2989

Zereini F, Wiseman C, Alt F, Messerschmidt J, Muller J, Urban H (2001a) Platinum and rhodium concentrations in airborne particulate matter in Germany from 1988 to 1998. Environ Sci Technol 35(10):1996–2000

Zereini F, Wiseman C, Beyer JM, Artelt S, Urban H (2001b) Platinum, lead and cerium concentrations of street particulate matter (Frankfurt am Main, Germany). J Soils Sediments 1 (3):188–195

Zereini F, Wiseman C, Puettmann W (2007) Changes in palladium, platinum, and rhodium concentrations, and their spatial distribution in soils along a major highway in Germany from 1994 to 2004. Environ Sci Technol 41(2):451–456

Accumulation and Distribution of Pt and Pd in Roadside Dust, Soil and Vegetation in Bulgaria

Valentina Lyubomirova and Rumyana Djingova

Abstract The concentration of Pt and Pd in Bulgaria resulting from traffic pollution has never been investigated. Samples of roadside dust, soils and *Taraxacum officinale*, collected along highways, some major and secondary roads and a smelter region during the summer of 2012 are analyzed by ICP-MS. The comparison to literature values shows that the average concentrations in road dusts along Bulgarian roads are lower than the average for Pt and around the average for Pd. Hotspots with concentrations of Pd up to 800 ng/g and Pt up to 220 ng/g were established. The transfer factors (plant/soil) determined in the present study and the results form the analysis of washed and unwashed plant samples give a serious indication that a substantial part of Pt and Pd, released into the environment enters the plants.

1 Introduction

The three-way catalytic converters, mainly using platinum, palladium and rhodium as active metals to control the vehicle pollutant emission have caused significant environmental increase of platinum metals. (Niemelä et al. 2005; Pan et al. 2013). A problem created by the use of these car catalysts is that a portion of the Platinum group elements (PGE) is released from the catalyst surface and they are spread and bioaccumulated into the environment. PGE emission rate and the proportions between Pt/Pd/Rh were found to be strongly correlated to several parameters like car speed, driving style (erratic stop-start flows), age and type of the catalytic converter (Zechmeister et al. 2006; Ward and Dudding 2004; Whiteley and Murray 2003).

PGE are released in small amounts, together with particles from the wash coat of the catalytic converter, due to fast-changing oxidative and reductive conditions, high temperatures and mechanical abrasion of the catalytic material. This has led to

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increasing concentrations of these metals in the environment, as has been documented in a number of studies (e.g. Gómez et al. 2000; Kanitsar et al. 2003; Leopold et al. 2008; Pan et al. 2009; Rauch et al. 2001; Wichmann et al. 2007; Zereini et al. 2001a, b; Zereini et al. 2007).

Previous studies have found elevated PGE levels in urban airborne dusts (e.g. Alsenz et al. 2009; Rauch et al. 2005; Wichmann et al. 2007; Zereini et al. 2012), road dusts and roadside soils (e.g. Boch et al. 2002; Cicchella et al. 2003, 2008; Djingova et al. 2003a, b; Ely et al. 2001; Hooda et al. 2007; Jarvis et al. 2001; Lee et al. 2012, Lesniewska et al. 2004; Ljubomirova et al. 2008; Morcelli et al. 2005; Qi et al. 2011; Schäfer et al. 1999; Wang et al. 2007), sediments (e.g. Rauch et al. 2004; Sutherland et al. 2007; Whiteley and Murray 2005), in plants grown on soil collected from road verges (Djingova et al. 2003a, b; Hooda et al. 2008; Schäfer et al. 1998; Zechmeister et al. 2005, 2006), and in sediments in local water bodies receiving runoff from road networks (Rauch and Hemond 2003).

However, the catalyst technology is continuously changing. According to previous reports, there is a rapid growth in the amounts of Pd used in catalytic converters since 1990s, for example from 22t in 1993 to 126t in 2009 (Zereini et al. 2012), and more than 90 % of the worldwide Rh supply were related to production of catalytic converters (Tuit et al. 2000). The catalyst industry is shifting from a Pt-Rh- to a Pd-Rh-version as the active layer of the monolithic catalyst body (Helmers et al. 1998). Cytotoxicity, mutagenic effects, bioaccumulation capability and other undesirable effects in living organisms have already been reported for environmental Pd (Gómez et al. 2003). Demand for palladium is intensifying worldwide as a result of (1) price-driven substitution of palladium for platinum in gasoline and diesel catalytic converter applications, (2) expanding automotive production and 3) ever more stringent governmental emission regulations. Observed environmental increases of Pd concentrations, reflect the increased its use in place of Pt in catalytic converters since the 1990s (Zereini et al. 2007). The chemical and noble metal extraction and processing industries are also important sources of PGE to the atmosphere (Barbante et al. 2001; Rauch et al. 2006; Reimann et al. 2006; Zereini et al. 1998). Automobile catalytic converters have, however, received the most attention as a primary contributor of PGE to the environment. Changes in proportions of PGE in catalyst products could also reflect certain development and improvement of catalyst technology in developing countries (Pan et al. 2013).

The highways in Bulgaria have a total length of 620 km (see Fig. 1). The longest one -A-1, Trakia (360 km) was finished July 2013 although parts of it are in exploitation since 1978 (the first 10 km from Sofia) and 1984 (the next 140 km from Sofia). The Hemus highway A-2 is still unfinished. 80 km from Sofia were built in the period 1984–1999, and 83 km from Varna to Sofia are in exploitation since 2005. The rest of the 418 route are still in the planning stage. The smallest highway is A-6, Lyulin (19 km) finished May 2011 and connects Sofia with Pernik. Soon the construction activities of highway Struma (A-3), planned to connect Sofia with Thessaloniki are expected to start. At present the heavy traffic there is running along a major road E-79.

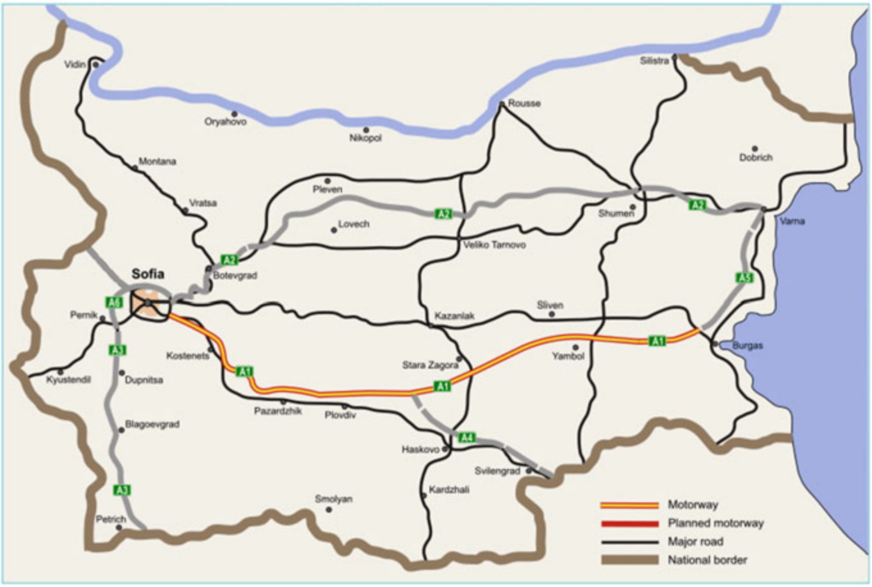

Fig. 1 Road map of Bulgaria

In the autumn of 2011 large scale screening of the distribution of PGE on the territory of Bulgaria has been performed. Samples of soils, road dust and vegetation were collected from 68 locations, situated in background regions (5 sampling sites), along the existing highways (10 locations) along major and secondary roads (30 sites), in towns (10 sites) and around two smelters. The analysis indicated that measurable concentrations of PGE were detected only along the highways, a limited number of secondary roads and around one of the smelters. Therefore in the autumn of 2012 sampling from these locations was performed.

The aim of the present study was: (i) monitoring and assessment of the environmental Pt and Pd concentration changes in Bulgaria as a consequence of human activities (ii) assessment of the bioaccumulation of PGEs in exposed plants under the new environmental concentrations.

2 Experimental

2.1 Samples and Sample Preparation

Samples of road dust, soil and vegetation (*Taraxacum officinale*) were collected along the oldest sections of highway A-1 (the first 150 km) and highway A-2 (the first 60 km). Samples were also collected along the 19 km long highway A-6;

a 10 km distributed along E-79, along the secondary roads 871 near Kazanlak and 55 near Veliko Tarnovo—Central Bulgaria (See Fig. 1) as well as around the Pb-Zn smelter in Kardzhali—South Bulgaria (see Fig. 1).

For comparison of the results samples of road dust, soil and *Taraxcum officinale* were collected from 10 sampling sites in the city of Ljubljana, Slovenia and a limited number of samples of soil and *Taraxacum officinale* from two parking places in Italy and Switzerland (E-35).

Everywhere the road dusts were sampled between the kerb and 50 cm into the road using plastic pan and brush. The soils were collected at a distance not more than 50 cm from the road edge and plants were samples from above the collected soil wherever *Taraxacum officinale* was available. The single sampling sites (within one location) were usually about 25 m long and depending on the specific conditions between 10 individual samples of each kind (for 871 and 55) and 25 (A-1, A-2 and A-6) were collected (soils at 0–5 cm depth).

Plants were sampled at the end of the flowering period by cutting with plastic scissors at 1 cm from the ground, as described in (Djingova and Kuleff 1994). All samples were collected in the autumn of 2012 after at least 20 days dry period. The plant samples were mechanically cleaned from dust and soil particles by blowing with air stream. Immediately after sampling, part of the foliage was washed thoroughly with tap water and rinsed with distilled water and another part was left unwashed. The plant samples were air dried in a clean room for 4–5 days, afterwards put in an oven for 4 h at 85 °C, ground in a polytetrafluoroethylene (PTFE) ball mill to fine powder and subjected to digestion. Approximately 0.3 g of the sample was placed in PTFE pressure vessels with 5 ml 65 % HNO_3 (Merck, suprapure) and 3 ml 30 % H_2O_2 (Merk, suprapure) The mixture was left to stay for 10 min and afterwards the closed vessels were introduced in the Multiwave digestion system using 5 steps of 5 min with the following power: 250, 400, 900, 300 and 0 W (vent, Tmax = 180 °C). The digested samples were quantitatively transferred in 50 mL polypropylene tubes by washing with double deionised water and diluted to 30 mL.

The soil and dust samples were hand cleaned from small stones, roots etc., sieved through 2-mm PTFE sieve and homogenized in a PTFE ball mill. About 0.3 g of the sample was placed in a Teflon pressure vessel and 6 mL aqua regia was added. The closed vessels were introduced in a microwave oven assisted sample digestion system and subjected to microwave digestion using six steps with the following power and time: 250 (2 min), 0 (2 min), 250 (5 min), 400 (4 min), 600 W (3 min) and 0 W (vent, Tmax = 180 °C). After cooling the content of the vessels was quantitatively transferred in 50 mL polypropylene tubes by washing with double deionised water. After centrifugation the supernatants were transferred to 100 mL polypropelene tubes and diluted to 50 ml with double deionized water.

2.2 Reagents

Suprapur chemicals and double deionised water (MilliQ) were used for preparing all solutions. Working standard solutions were prepared from single element calibration solutions (Merck) by appropriate dilution in the respective matrix. Blank determinations were run by using the same reagents in equal quantities as for the plants and the soil/dust samples.

2.3 Instrumentation

Analysis of the samples was carried out using a Perkin Elmer SCIEX DRC-e ICP-MS system with cross-flow nebulizer. The spectrometer was optimized to provide minimal values of the ratios CeO^+/Ce^+ and Ba^{2+}/Ba^+ and optimal intensity of the analytes. External calibration was performed. The calibration coefficients for all calibration curves were at least 0.99.

The optimum ICP-MS measurement conditions and isotopes used in the analysis of the elements of interest are given in Table 1. The spectrometer is equipped with a dynamic reaction cell (DRC) for removal of multi-element interferences using methane as a reaction gas.

The microwave digestion of the samples was performed with Microwave Reaction System (Anton Paar, Multiwave 3000).

Table 1 Measurement conditions for ICP-MS (Perkin-Elmer SCIEX DRC-e)

Argon plasma gas flow		15 L min^{-1}
Auxiliary gas flow		1.20 L min^{-1}
Nebulizer gas flow		0.90 L min^{-1}
Lens voltage		6.00 V
ICP RF power		1,100 W
Pulse stage voltage		950 V
Dwell time		50 ms
Acquisition mode		Peak hop
Peak pattern		One pint per mass at maximum peak
Sweeps/readings		8
Reading/replicate		1
Sample uptake rate		2 mL min^{-1}
Number of runs		6
Rinse time		180 s
Rinse solution		3 % HNO_3
Measured masses		Pd-105, Pd-108, Pt-194, Pt-195
DRC parameters	Pd-105	Cell gas flow-0.2 L min^{-1}; RPq-0.6 V
	Pd-108	Cell gas flow-0.2 L min^{-1}; RPq-0.65 V

2.4 Spectral Interferences

The spectral interferences in the ICP-MS determination of Pt and Pd are well known and much discussed. The spectral overlap of HfO^+ with all Pt isotopes and of ZrO^+, YO^+, SrO^+ Mo^+ and Cd isotopes with Pd were extensively investigated and evaluated in different matrices (see e.g. Djingova et al. 2003a).

Depending on the analyte two different strategies for interferences removal were adopted, including reaction gas and/or correction equations.

The following equation was used for correction of the interference of HfO^+ on Pt (Djingova et al. 2003a):

$$S_{\mathrm{corr}} = S_{\mathrm{meas}} - (S_{\mathrm{inter}}\, A)$$

where S_{corr} is the corrected signal of the analyte, S_{meas} is the measured signal, S_{inter} is the signal of the interfering element and A is the % formation of the respective interfering species (e.g. oxide). The values of A are determined in model solutions with appropriate concentration of the interfering element and measured at the working conditions in Table 1. Pd was determined using the DRC mode with methane as reaction gas.

2.5 Quality Control

Quality control was performed using JSd-2 (Stream sediment, Geological Survey of Japan), BCR 723 and two in- house laboratory standards (dust and plant). The accuracy was better than 5 % for Pt and 8 % for Pd. All samples were analyzed in triplicate and at the start and end of each batch (10 samples) blank and standard samples were assayed. The detection limit was 0.01 ng/g for Pt and 0.05 ng/g for Pd.

3 Results and Discussion

3.1 Road Dust Samples

Table 2 presents the average, minimum and maximum concentrations obtained from the analysis of the road dust samples. For comparison results from the analysis of the samples collected in the city of Ljubljana (Slovenia) in 2012; A-2, the suburbs of Berlin (Germany) and suburbs of Warsaw (Poland), collected 2009 and literature values for the period 1998–2006 (Jackson et al. 2007) are given.

The results show that in all investigated locations in Bulgaria (but the smelter region) as well as in the samples from Ljubljana, Berlin and Warsaw the concentrations of Pd are higher than of Pt following the latest tendencies to substitute Pt

Table 2 Concentration of Pt and Pd [ng/g] in road dust samples

	Pt			Pd		
	min	average	max	min	average	max
Highway A-1	32	30.6	59	60	201.9	380.8
Highway A-2	24	73	204	138	209	247
Highway A-6	1.2	7	32	7.2	59	88
E-79	14	72.7	216	24	370	808
871	18	28	62	30	62	148
55	0.42	55	90	51	131	402
Smelter	16	50.5	85	8	28	50
A-2 (2009)[a]		21.5			53	
Ljubljana 2012	12.8	33	56.9	36.6	52.6	75.6
Berlin 2009[a]		55.6			97.6	
Warsaw 2009[a]		12.3			72.6	
Literature values[b]	0.4	128.3	2252	0	106.4	556.3

[a] Samples from a single location

[b] Jackson et al. (2007)

with Pd in the catalytic convertors. The trend in the concentrations of both elements for the investigated locations in Bulgaria is similar, the correlation coefficient is 0.89. The highest concentrations for Pt and Pd were established along E-79 where not only the traffic is very intensive, being the major road connecting Bulgaria and Greece, but very often intensive traffic jams with erratic stop-and-start mode take place. This explanation is confirmed by the fact that the highest concentrations of Pd (up to 800 ng/g) and Pt along E-79 are established nearest to the border and before tunnels where speed limits exist. Expectedly the two highways A-1 and A-2 have second highest concentrations while amazingly the lowest values were found along A-6. Unexpected hotspot was established along the local secondary road 55 (Pd: 413 ng/g) connecting Veliko Tarnovo and a small resort village (see Fig. 1). The traffic density is highest along the three highways and E-79 and lowest along 55. The traffic conditions permit highest speed along A-6 (where lowest concentrations of Pt and Pd were established) about 140 km/h and lowest along 55. The location where extremely high values for Pt and especially Pd (see Table 2) along 55 were determined is a steep curve where the maximum permitted speed is 30 km/h. These results are an indication that more important factors for the release of PGE to the environment than the traffic density might be slow speed and stop-and-go traffic (Hooda et al. 2007; Wichmann et al. 2007).

The smelter region is characterized by higher Pt concentration than Pd which is an indication for a different type of anthropogenic influence presumably the smelter.

The comparison to earlier results from a single site along A-2 (same sampling location) in 2009, shows about 3.5 times increase in the concentrations of both elements. Obviously for 3 years the increase in PGE concentration along the highway is significant. The comparison to literature values (Jackson et al. 2007) and results from the analysis of samples from Ljubljana, Berlin and Warsaw show that the average concentrations along Bulgarian roads are lower than the average summarized by Jackson et al. (2007) for Pt and around the average for Pd. The slightly higher concentrations in comparison to Berlin and Warsaw are due to the different type of sampling locations-highways or major roads and city suburbs and probably to the difference in time of sampling.

Although the production and use of leaded gasoline is forbidden in Bulgaria since 2004, the majority of cars (more than 70 %) are older than 15 years and if they have catalytic converters at all, these converters are too old to emit PGE. Nevertheless the concentrations obtained in this study are around the values measured in different European countries.

3.2 Soil Samples

The concentrations of Pt and Pd in the soil samples are lower than in the road dust but the difference is not substantial. The concentration of Pt is between 1.4 and 2.8 times lower than in the respective road dust and only for 55 the ratio is 4.4. For Pd the ratio Pd_{dust}/Pd_{soil} varies between 1.1 and 4.9. The trend in the concentrations of both elements in the soil along the highways is similar as presented in Fig. 2. The soils in the smelter region have higher concentrations of Pt than Pd which corresponds to the results from the dust analysis.

Comparison to the results from the analysis of soil samples from Ljubljana, Italy and Switzerland is presented also in Fig. 2. The concentrations of Pt and especially of Pd in Ljubljana soils are higher and similar to those along E-79. This similarity might be mostly due to the fact that sampling was performed in the city center

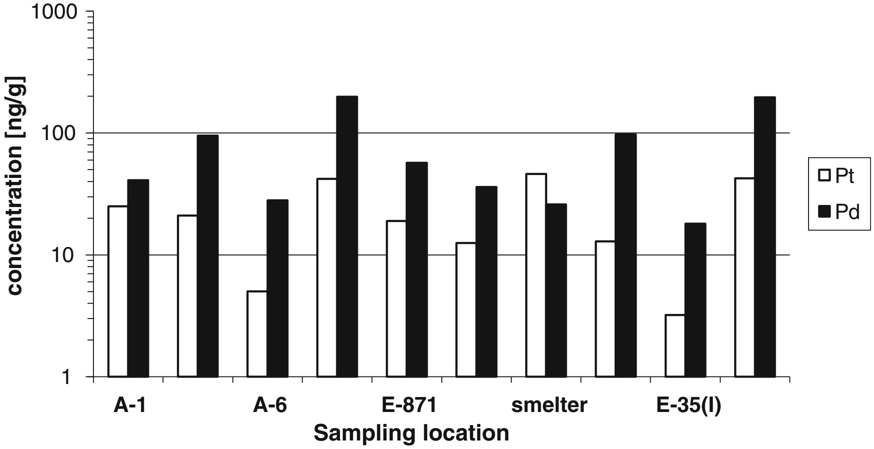

Fig. 2 Concentrations of Pt and Pd [ng/g] in soils from the investigated locations

where not only traffic is intensive but slow speed and stop and go conditions are typical. This was not established in the case of road dusts (see Table 2). However it must be kept in mind that the Bulgarian samples were collected after a prolonged dry period while in Ljubljana often street washing is done leading to removal of road dust but the soil continues to accumulate. This is why the soils in Ljubljana have higher concentrations of PGE than the dusts while along the Bulgarian roads this is not the case after a long lasting dry whether. The concentrations in the samples from Switzerland are similar while those from Italy are considerably lower than in the Bulgarian soils. The parking place in Italy (E-35 near the Swiss border) was situated aside from the road and soil and plants were available rather far from the traffic. This explains the difference to the results from Swiss samples, the site in Switzerland being situated 10 km away on the other side of the border.

3.3 Plant Samples

Figures 3 and 4 present a comparison of the concentrations of Pt and Pd in the investigated dust, soil and *Taraxacum officinale* (washed leaves) samples. Except for the samples from road 55 in the other locations the trend in the concentrations is the same for the three types of samples, the smelter region inclusive. This result is in a very good agreement to earlier investigations using *Taraxacum officinale* to assess PGE pollution along German highways (Djingova et al. 2003b). Correlation between soil and plant concentrations of Pt (though resulting from mining activities) was established also in (Rauch and Fatoki 2013) for several grass species while Hooda et al. 2007 and Pan et al. 2009 do not establish soil/plant correlation. Obviously the reason might be the plant species chosen for the investigation. It is

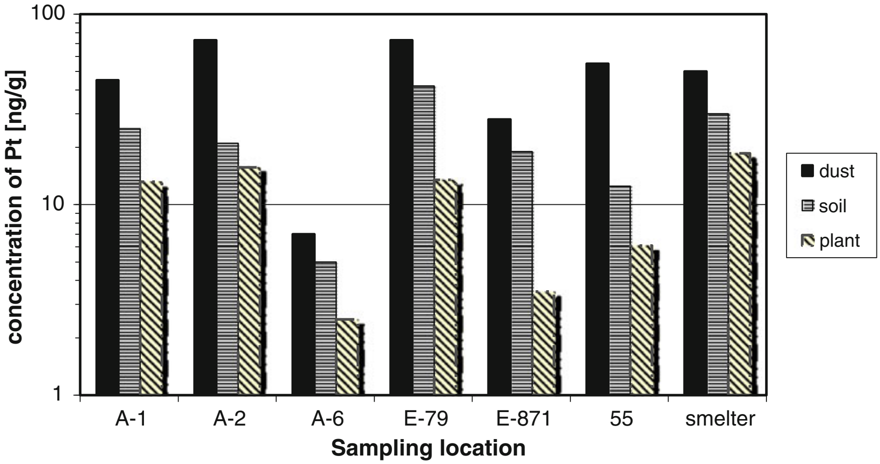

Fig. 3 Concentration of Pt [ng/g] in the investigated dust, soil and plant samples

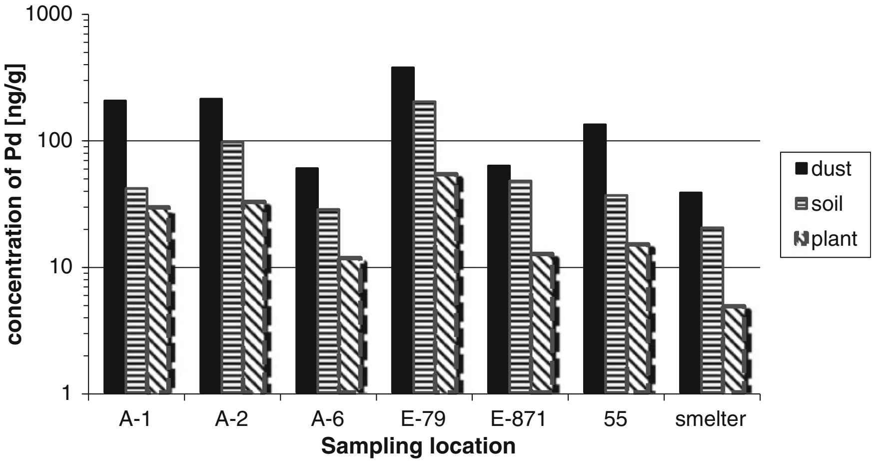

Fig. 4 Concentration of Pd [ng/g] in the investigated dust, soil and plant samples

well known that not all plant species reflect properly environmental conditions (Markert 1993). While *Taraxcum officilale* has been standardized as biomonitor of environmental pollution (Djingova and Kuleff 1993) and the correspondence in its concentration and PGE pollution has been demonstrated (Djingova et al. 2003b) this may not be the case with *Dactylis glomerata* (Hooda et al. 2007) and the undefined plant species, analyzed in (Pan et al. 2009). The difference established for the sampling location along road 55 is between the dust and soil concentrations which are defined by the relief of the sampling site. Soil and plant samples were not taken parallel to the road dust but several meters aside.

Although there are certain indications that the behavior of Pt and Pd differ in respect to plant uptake we did not establish such difference. The transfer factors (ratio between the concentration of the element in the plant to its concentration in the soil) indicate a rather high degree of uptake. The average value for the transfer factor for Pt in Bulgarian samples is (0.26 ± 0.12), and for Pd is (0.43 ± 0.18) and the results are very consistent. These values correspond to the assumption that Pd is transferred more easily to the plant in comparison to Pt. The transfer factors established for the samples from Italy and Switzerland are very similar to the Bulgarian samples: 0.11–0.37 for Pt and 0.22–0.48 for Pd which confirms the results obtained for the Bulgarian samples. The ratio for Ljubljana samples are slightly lower for Pt (0.02–0.2) and very similar for Pd (0.11–0.42). This result is a strong indication about the mobility of PGE in the environment and the respective transfer along the food chain. To investigate further the incorporation of PGE into the plant, unwashed leaves were analyzed as well (as described in the Experimental part). The results are presented in Fig. 5. The concentrations in the washed samples for Pt are between 30 and 88 % and for Pd - between 45 and 90 % from the concentration of the unwashed leaves. Similar results were obtained earlier with *Taraxacum officinale* (Djingova et al. 2003b) and by (Hooda et al. 2007; Pan et al. 2009; Rauch and Fatoki 2013)

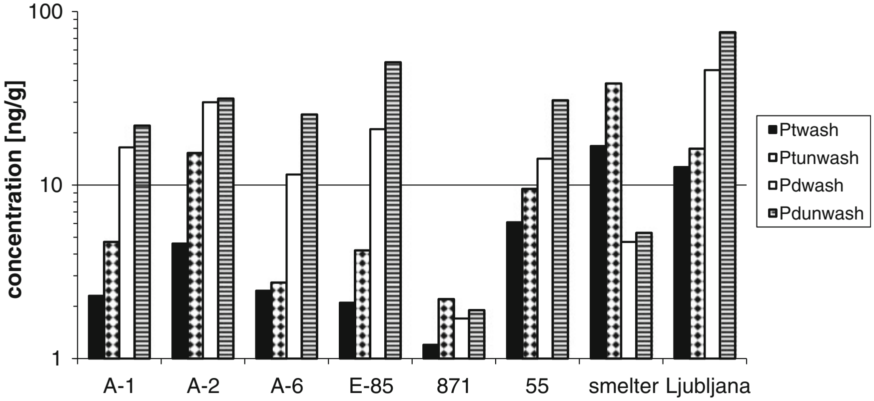

Fig. 5 Concentrations of Pt and Pd [ng/g] in washed and unwashed leaves of *Taraxacum officinale*

with different species. Since all *Taraxacum* samples have been collected after of at least 20 days dry period it might be assumed that a substantial part of the PGE enters the plant which again is a strong confirmation of the obtained rather high results for the transfer factors.

4 Conclusion

The results from the present investigation show uneven distribution of PGE on the territory of Bulgaria. While in background regions, towns and along the majority of secondary roads the concentrations of PGE are still below the detection limit, along highways some major and secondary roads values up to 800 ng/g Pd and 200 ng/g Pt were established in road dust. The results indicate that more important than traffic density and velocity seem to be traffic jams, slow speed and stop-and-go traffic. The concentrations of Pt and Pd in dust, soil and *Taraxacum officinale* have the same trend along the investigated locations. The plant/soil transfer factors and the small difference in the concentrations of washed and unwashed leaves of *Taraxacum officinale* indicate significant transfer of Pt and Pd to the plants. A comparison to samples from other European countries prove medium PGE pollution in Bulgaria and confirm the results obtained for the transfer in the system plant/soil.

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References

Alsenz H, Zereini F, Wiseman CLS, Püttmann W (2009) Anal Bioanal Chem 395:1919–1927

Barbante C, Veysseyre A, Ferrari C, van de Velde K, Morel C, Capodoglio G, Cescon P, Scarponi G, Boutron CF (2001) Environ Sci Technol 35:835–839

Boch K, Shuster M, Risse G, Schwarzer M (2002) Anal Chim Acta 459:257–265

Cicchella D, Fedele L, De Vivo B, Albanese S, Lima A (2008) Geochem Explor Environ Anal 8:31–40

Cicchella D, De Vivo B, Lima A (2003) Sci Total Environ 308:121–131

Djingova R, Kuleff I (1994) In: Markert B (ed) Environmental sampling for trace analysis. VCH, Weinheim, pp 395–414

Djingova R, Kuleff I (1993) In: Markert B (ed) Plants as biomonitors. VCH, Weinheim, pp 435–457

Djingova R, Heidenreich H, Kovacheva P, Markert B (2003a) Anal Chim Acta 489:245–251

Djingova, R. Kovacheva P., Wagner G., Markert B., Sci. Total Environ., 2003b, 308, 235–246

Ely JC, Neal CR, Kulpa CR, Schneegurt MA, Seidler JA, Jain JC (2001) Environ Sci Technol 35:3816–3822

Gómez MB, Gómez MM, Palacios MA (2003) J Anal At Spectrom 18:80–83

Gómez MB, Gomez MM, Palacios MA (2000) Anal Chim Acta 404:285–294

Helmers E, Schwarzer M, Schuster M (1998) Environ Sci Pollut Res 5:44–50

Hooda PS, Miller A, Edwards AC (2007) Sci Total Environ 384:384–392

Hooda PS, Miller A, Edwards AC (2008) Environ Geochem Health 30:135–139

Jackson MT, Sampson J, Prichard HM (2007) Sci Total Environ 385:117–131

Jarvis KE, Parry SJ, Piper JM (2001) Environ Sci Technol 35:1031–1036

Kanitsar K, Koellensperger G, Hann S, Limbeck A, Puxbaum H, Stingeder G (2003) J Anal At Spectrom 18:239–246

Lee HY, Chon HT, Sager M, Marton L (2012) Environ Geochem Health 34:5–12

Leopold K, Maier M, Weber S, Schuster M (2008) Environ Pollut 156:341–347

Lesniewska BA, Godlewska-Zylkiewicz B, Bocca B, Caimi S, Caroli S, Hulanicki A (2004) Sci Total Environ 321:93–104

Ljubomirova V, Djingova R, van Elteren JT, Veber M, Kowalkowski T, Buszewski B (2008) Intern J Environ Anal Chem 88:499–512

Markert B (1993) Plants as biomonitors. VCH, Weinheim

Morcelli CPR, Figueiredo AMG, Sarkis JES, Enzweiler J, Kakazu M, Sigolo JB (2005) Sci Total Environ 345:81–91

Niemelä M, Kola H, Perämäki P, Piispanen J, Poikolainen J (2005) Microchim Acta 150:211–217

Pan SH, Sun YL, Zhang G, Chakraborty P (2013) J Geochem Explor 128:153–157

Pan SH, Zhang G, Sun YL, Chakraborty P (2009) Sci Total Environ 407:4248–4252

Qi L, Zhou MF, Zhao Z, Hu J, Huang Y (2011) Environ Earth Sci 64:1683–1692

Rauch S, Ehrenbrink BP, Molina LT, Molina MJ, Ramos R, Hemond HF (2006) Environ Sci Technol 40:7554–7560

Rauch S, Fatoki OS (2013) Water Air Soil Pollut 224:1395–1402

Rauch S, Hemond HF (2003) Environ Sci Technol 37:3283–3288

Rauch S, Hemond HF, Peucker-Ehrenbrink B (2004) Environ Sci Technol 38:396–402

Rauch S, Hemond HF, Peucker-Ehrenbrink B, Ek KH, Morrison GM (2005) Environ Sci Technol 39:9464–9470

Rauch S, Lu M, Morrison GM (2001) Environ Sci Technol 35:595–599

Reimann C, Niskavaara H (2006) In: Zereini F., Alt F. (eds) Palladium emissions in the environment: analytical methods, environmental assessment and health effects. Springer, Heidelberg, p 53–70

Schäfer J, Eckhardt JD, Berner ZA, Stüben D (1999) Environ Sci Technol 33:3166–3170

Schäfer J, Hannker D, Eckhardt JD, Stüben D (1998) Sci Total Environ 215:59–67

Sutherland RA, Pearson DG, Ottley CJ (2007) Appl Geochem 22:1485–1501

Tuit CB, Ravizza GE, Bothner MH (2000) Environ Sci Technol 34:927–932
Wang J, Zhu RH, Shi YZ (2007) J Environ Sci 19:29–34
Ward NI, Dudding LM (2004) Sci Total Environ 335:457–463
Whiteley JD, Murray F (2003) Sci Total Environ 317:121–135
Whiteley JD, Murray F (2005) Sci Total Environ 341:199–209
Wichmann H, Anquandah GAK, Schmidt C, Zachmann D, Bahadir M (2007) Sci Total Environ 388:121–127
Zechmeister HG, Hagendorfer H, Hohenwallner D, Hanus-Illnar A, Riss A (2006) Atmos Environ 40:7720–7732
Zechmeister HG, Hohenwallner D, Riss A, Hanus-Illnar A (2005) Environ Pollut 138:238–249
Zereini F, Alsenz H, Wiseman CLS, Püttmann W, Reimer E, Schleyer R, Bieber E, Wallasch M (2012) Sci Total Environ 416:261–268
Zereini F, Dirksen F, Skerstupp B, Urban H (1998) Environ Sci Pollut Res 5:223–230
Zereini F, Skerstupp B, Rankenburg K, Dirksen F, Beyer JM, Claus T, Urnan H (2001a) J Soils Sed 1:44–49
Zereini F, Wiseman C, Alt F, Messerschmidt J, Müller J, Urban H (2001b) Environ Sci Technol 35:1996–2000
Zereini F, Wiseman C, Püttmann W (2007) Environ Sci Technol 41:451–456

Increase of the Environmental Pt Concentration in the Metropolitan Area of Mexico City Associated to the Use of Automobile Catalytic Converters

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Abstract This work shows the results of de investigations concerning Pt concentration in the environment of Mexico City, product of the impact of the use of catalytic converters in the urban area. This research was carried out by assessing Pt concentration in dust samples and PM2.5 collected in the metropolitan area of Mexico City. Dust samples were divided in “road dust” and “urban dust” according to vehicle traffic exposure. Pt concentration in road dust samples, exposed to high traffic density, range from 37.7 to 231 $\mu g\ kg^{-1}$ (mean 112 $\mu g\ kg^{-1}$), whereas Pt concentration found in urban dust, collected in areas with low traffic density, varied between 26.4 and 86.6 $\mu g\ kg^{-1}$ (mean 57 $\mu g\ kg^{-1}$). PM2.5 samples were collected in five sites of the urban area during three different seasons (dry-warm, rainy, dry-cold). Results do not show significant spatial or temporal variation. Pt concentration ranges from 1 to 79 $pg\ m^{-3}$. The comparison of Pt concentration in dust and $PM_{2.5}$ samples presented here, with data reported for other urban areas, as well as with data previously reported for PM_{10} collected in 1991 and 2003 for the metropolitan area of Mexico City, allows to conclude a significant increase of Pt in this urban environment.

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1 Introduction

Platinum is one of the active components of automobile catalysts, which convert noxious gas emissions to more benign forms. In recent years it has been recognized that automobile catalysts as the main source of antrophogenic Pt in the environment. Numerous studies have highlighted the enrichment of Pt in the environment caused by their release as a result of the abrasion of these catalytic converters. Furthermore, their release depends on the operation conditions and the age of the catalytic converter.

In urban areas, assessment of Pt pollution has been frequently performed by analyzing road and urban dust, because they represent an accumulation of solid particles containing metals from a variety of sources mainly vehicular traffic (Gomez et al. 2002; Kan and Tanner 2004; Wang et al. 2007; Qi et al. 2011; Spada et al. 2012; Pan et al. 2013) and may also act as a source to atmospheric pollution through resuspention (Laschober et al. 2004; Limbeck et al. 2007; Spada et al. 2012).

On the other hand, the identification of the adverse human health effects induced by the exposure to airborne particulate matter (Pope et al. 2002) has brought increasing concern/interest in studying their concentration. An appropriate assessment of the environmental exposure to Pt in airborne particulate matter has been reported (Gomez et al. 2001; Rauch et al. 2001, 2006; Kanistar et al. 2003; Zereini et al. 2004, 2012; Bocca et al. 2006; Morton-Bermea et al. 2014. Rauch et al. (2006) and Limbeck et al. (2007) concluded that Pt average values for $PM_{2.5}$ were lower than for PM_{10}. In the same way, Zereini et al. 2012 observed that PGE concentrations declined with the size of the particle fraction, from PM_{10} to PM_1.

For Mexico, the investigation of Pt abundances in urban environments is scares. There are only few reports regarding Pt concentration in the environment of the metropolitan area of Mexico City. Morton et al. 2001 reported PGE concentration en urban topsoils. Afterward, Rauch et al. 2006 reported data related to the Pt, Pd and Rh concentration in PM_{10} collected in representative sites in Mexico City. Recently, Morton-Bermea et al. 2014 presented a spatial and temporal distribution of Pt in $PM_{2.5}$ collected at five sites in the metropolitan area of Mexico City. These studies show a worrying increase in the concentration of Pt in the environment of MAMC since the mandatory introduction of automobile catalysts in 1991; because this increasing trend is expected to continue, it results relevant to monitor and assess the temporal and spatial distribution of Pt. With this frame, the aim of this study is to conduct a comprehensive assessment of the impact of the use of catalysts in the metropolitan area of Mexico City environment, using urban and road dust samples, as well as $PM_{2.5}$ samples taken in the studied area.

2 Experimental

2.1 Study Area

The studied zone was the metropolitan area of Mexico City (MAMC) including its suburban areas. The MAMC, with more than 20 million inhabitants, covers a total land area of 1,200 km^2 surrounded by mountains ay the South, East and West sides and completely open at the North side. The mean annual temperature is 16 °C and the average annual rainfall is 660 mm. The MAMC has experienced a substantial uncontrolled development over the past 30 years. In general, the city is high urbanized and industrialized with high traffic density and with most land area devoted to building, road surfaces and paving (INEGI 2011).

2.2 Sampling and Analytical Treatment

2.2.1 Urban and Road Dust

A sampling campaign was carried out during May 2013. A total of 30 road dust samples were collected in the southern part of MAMC from road subways at junctions of avenues with more than three lanes each (ca. 3,000 vehicles h^{-1}). Furthermore, 10 urban dust samples were taken from paved surfaces in representative locations of the MAMC, with a less intense exposure to vehicular traffic than road dust samples (<500 vehicles h^{-1}).

Dust was swept with a clean plastic brush, collected with a clean plastic scoop and placed in a clean zip-lock plastic bag. All dust samples were dried at room temperature for 48 h and at 60 °C during further 48 h. Approximately 100 g sample were grounded to 200 mesh size using an agate mortar.

About 0.2 g accurately weighted dust sample were placed in Teflon vessels and an acid mixture was added (8 ml agua regia and 2 ml HF). The mixture was allowed to stand overnight. 2 ml HCl were added and a microwave digestion procedure was applied using an EHTOS One (Milestone) microwave oven. The digestion temperature was ramped from room temperature to 180 °C in 20 min and then maintained for 15 min. Samples were taken to dryness and to ensure the full removal of HF, 2 ml HCl were added and evaporated twice. After cooling, the digested sample was diluted to 50 ml with 2 % HNO_3 (v/v).

2.2.2 $PM_{2.5}$

The sampling program was conducted in 2011 during three different seasons (April: dry-warm season; August: rainy season; December (dry-cold season). High-Vol equipments (Tisch and Anderson General Metal Works) previously calibrated according to Federal Register (1987) were used to collect simultaneously $PM_{2.5}$ at five sites selected sites in the MAMC, representatives of different pollution sources. A flow rate of 1.13 ± 10 % m^3 min^{-1} was used. Samples were collected every sixth days for 24 h on Teflon-impregnated glass fiber filter (20.4 cm × 25.2 cm). Filters were wrapped in aluminum foil and then kept in zip-lock bags to be transported.

Loaded filter samples were digested using a ETHOS ONE (Millipore) microwave oven, equipped with a rotor system for 10 Teflon vessels (PRO-24). About 0.1 g filter material was placed in Teflon vessels where 8 ml agua regia, 1 ml HF and 2 ml HCl and left to stand overnight. The digestion temperature ranged from room temperature to 180 °C in 20 min and then maintained for 20 min. The resulting solution was transferred to a Teflon vessel (100 ml) and evaporated to dryness. To ensure full removal of HF, 3 ml HCl were added to the digestate and evaporated twice. The final digested sample was taken to a volume of 10 mL with 2 % HNO_3 (v/v).

2.3 ICP-MS Analysis and Quality Control

All measurements were carried out using an ICP-MS (iCAP Q, Thermo Scientific, Germany), in the Instituto de Geofísica of Universidad Nacional Autónoma de México. The spectral interferences produced by matrix components in the ICP-MS analytical determination of Ptare eliminated by the application of kinetic energy discrimination and a collision cell adapted to the ICP-MS. Instrumental drift were corrected using ^{115}In as internal standard prepared from a certified stock solution of 1,000 mg L^{-1} (Merck, Germany). Detection limits were calculated as three times the blank filter standard deviation. The potential of ICP-MS with dynamic reaction cell and cell collision unit for suppressing polyatomic interferences, as well as the recovery of analysis, were tested with road dust reference material BCR-723 (Standards, Measurements and Testing Program, of the European Union). Reference materials were prepared in the same way as collected samples. Fourteen BCR-723 aliquots was prepared and analyzed in the same way as road and urban dust. In the case of $PM_{2.5}$, twenty two replicates of glass fiber filter were loaded with about 20 mg of BCR-723 and subjected to microwave assisted digestion procedure in the same way as collected $PM_{2.5}$ samples before analysis.

The quality of the analytical procedure for the determination of Pt in road and urban dust, as well as in $PM_{2.5}$, was evaluated in terms of recovery rate using BCR-723. The quantitative recovery was 97.3 % (n = 14) and precision 4.8 %. In $PM_{2.5}$, calculated recovery rate was 69.7 % and precision was calculated as 7.1 % (n = 22). In all analyzed samples, Pt concentration was higher than detection and quantification limits (0.007 and 0.025 μg L^{-1}). Recovery rates were used to adjust final Pt concentration in road and urban dust, and in air ($PM_{2.5}$).

3 Results

3.1 Road and Urban Dust

Table 1 shows Pt concentration data of the analyzed road and urban dust samples compared with Pt concentrations reported from other studies in several parts of the world (road and urban dust). It is shown that average Pt concentration in road dust samples obtained in this study is about 2.5 times higher than in urban dust. This may be the result of the protection from the meteorological conditions and dispersion which results in the covered section of the roadway junctions (road dust samples) in comparison with samples taken from free surfaces areas (urban dust samples).

Comparison of the obtained results with data reported for other urban areas are very interesting. Pt concentration in urban dust samples from the studied area is lower than Pt concentration reported in samples from Hong Kong and Macao, where catalytic converters were introduced to vehicles as early as in European countries (Pan et al. 2013). On the other hand, obtained Pt concentrations are of the same magnitude as Pt concentrations reported for samples taken in Beijing and Shanghai, where catalytic converters have been used "for a short time period" (Pan et al. 2013). This may be a consequence of a similar urban development history, in terms of traffic density and/or the rapid increase of vehicles with catalytic converters.

The lower Pt concentration data reported by Spada et al. 2012 for road dust samples taken in the Houston metropolitan area is probably related to the lower automobile number than in Mexico City.

As well as for urban dust, Pt concentration in road dust samples taken in Beijing (Wang et al. 2007) are similar to those obtained in this study while those found in

Table 1 Comparison of Pt concentration in road and urban dust obtained in this study with data reported for other urban areas

	Location	Year	Road dust (μg kg^{-1})	Urban dust (μg kg^{-1})
This work	Mexico City	2013	37.7–231.1 (mean 112)	26.4–86.6 (mean 57)
Pan et al. (2013)	Beijing	2007–2009		12.3–84.6 (mean 45.2)
	Shanghai			7.9–54.9 (mean 22)
	Guangzou			13.8–315 (mean 86.1)
	Hong Kong			35.5–268 (mean 112)
	Macao			28.4–385 (mean 113)
Spada et al. (2012)	Houston	2012	35–131	
Wang et al. (2007)	Beijing	2002–2004	3.96–356.3 (mean 97.2)	
Kan and Tanner (2004)	Hong Kong	2004	111–478 (mean 196.1)	

dust samples taken in Hong Kong are higher. These data further suggest that the impact of the use of catalytic conversers in MAMC is comparable to that in Beijing and Shanghai.

3.2 $PM_{2.5}$

Spatial and seasonal distribution of Pt concentration in the analyzed $PM_{2.5}$ samples is shown in Table 2. Mean concentration of Pt in all analyzed samples is 39 pg m^3. The spatial analysis of the results when all season are considered shows that Pt concentration in SW is significantly higher compared to NW and to C ($p < 0.05$). The seasonal comparison of Pt concentration shows that Pt mean concentration was significantly higher in rainy season.

The assessment of these results shows that the highest Pt concentration was found at SW, mainly a residential area, which may be the result of higher traffic density conditions and/or a higher percentage of vehicles using catalytic converters.

In a previous publication (Morton-Bermea et al. 2014) we present a comparison of Pt concentrations in $PM_{2.5}$ obtained in this study (39 pg m^{-3}) with data reported for other urban Analyzed samples in this study show an evident Pt enrichment compared to Pt concentration found in $PM_{2.5}$ collected in Göteborg, Sweden (Rauch et al. 2001), Vienne, Austria (Limbeck et al. 2007) and Frankfurt, Germany (Zeirini et al. 2012) were Pt concentration are 5.4, 12 and 9.4 pg m^{-3} respectively. This can be clearly related to the intensity of traffic density.

Table 2 Pt concentration in $PM_{2.5}$ (pg m^{-3}) at MAMC

	n	Mean	Median	Minimum	Maximum	SD
		pg m^{-3}				
MAMC	73	39	38	1	79	17
Spatial distribution						
Site		pg m^{-3}				
NW	14	31	31	1	46	14
NE	14	39	36	9	74	18
C	16	34	37	12	56	13
SW	14	50	46	34	79	16
SE	15	43	41	17	76	21
Seasonal distribution						
Season		pg m^{-3}				
Dry_warm	22	46	42	12	72	22
Rainy	28	54	52	27	79	18
Dry_cold	23	38	34	1	71	17

n Number of observations, *SD* Standard deviation

Unfortunately there is no previous data of Pt in $PM_{2.5}$ in the studied area. Rauch et al. 2006 carried out an analytical determination of Pt concentration in PM_{10} collected in 1991 in La Merced (corresponding to the site called Central, C in this study) and in samples collected in five sites in the urban area during 2003. They report a mean Pt concentration of 1.9 and 9.3 pg m^{-3} respectively. Considering that it has been previously reported that Pt concentration decline whit the size of particulate fraction (Rauch et al. 2001; Limbeck et al. 2007; Zereini et al. 2012) it would be expected that Pt concentration in $PM_{2.5}$ were lower than Pt concentration in PM_{10} collected in 1991 and 2003 reported by Rauch et al. 2006. This fact evidences the considerable increase of Pt concentration in the air environment of the studied area since 1991.

4 Conclusion

High levels of Pt in road and urban dust, as well as the demonstrated increase in $PM_{2.5}$ in the MAMC, demonstrate the impact of more of 4 million vehicles with catalytic converter in the MAMC.

The assessment of the results obtained in this study and the comparison with those previously reported, allows to conclude that the magnitude of Pt concentration in urban and road dust obtained in this study is comparable to those reported for other mega cities like Beijing and Shanghai, probably related to similar traffic conditions as well as to the length of time using catalytic converters. However, these Pt concentrations are lower than those reported for Hong Kong and Macao, where vehicles were equipped with catalytic converters since late 1980s.

On the other side, Pt concentration found in $PM_{2.5}$ collected in 2011 are higher than those reported for other urban areas, (Göteboug, Vienna, Frankfurt) clearly exposed to lower traffic intensities. A significant increase in observed in Pt concentration in $PM_{2.5}$ compared with results obtained in PM_{10} collected in 1991 and 2003 in the same area. This is particularly relevant since $PM_{2.5}$ represent the inhalable fraction that has been linked to adverse effects to human health.

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References

Bocca B, Caimi S, Smichowski P, Gomez D, Caroli S (2006) Monitoring Pt and Rh in urban aerosols from Buenos Aires, Argentina. Sci Total Environ 358:255–264

Federal Register (1987) 40 CFR Appendix J to Part 50—Reference method for the determination of particulate matter as PM_{10} in the atmosphere

Gomez B, Gomez M, Sanchez JL, Fernandez R, Palacios MA (2001) Platinum and rhodium distribution in airborne particulate matter and road dust. Sci Total Environ 269:131–144

Gomez B, Palacios MA, Gomez M, Sanchez JL, Morrison G, Rauch S, McLeod C, Ma R, Caroli S, Alimonti A, Petrucci F, Bocca B, Schramel P, Zischka M, Petterson C, Wass U (2002) Levels and risk assessment for humans and ecosystems of platinum-group elements in the airborne particles and road dust of some European cities. Sci Total Environ 299:1–19

INEGI Instituto Nacional de Estadística y Geografía (2011) Cuaderno Estadístico de la Zona Metropolitana del Valle de México. http://www.inegi.org.mx/est/contenidos/espanol/sistemas/cezm11/estatal/default.htm. Accessed Nov 2013

Kan SF, Tanner PA (2004) Determination of platinum in roadside dust samples by dynamic reaction cell-inductively coupled plasma-mass spectrometry. J Anal At Spectrom 19:639–643

Kanitsar K, Koellensperger G, Hann S, Limbeck A, Puxbaum H, Stingeder G (2003) Determination of Pt, Pd and Rh by inductively coupled plasma sector field mass spectrometry (ICP-SFMS) in size-classified urban aerosol samples. J Anal At Spectrom 18:239–246

Laschober Ch, Limbeck A, Renl J, Puxbaum H (2004) Particulate emissions from on-road vehicles in the Kaisermühlen-tunnel (Vienna, Austria). Atmo Environ 38:2187–2195

Limbeck A, Puls C, Handler M (2007) Platinum and Palladium emissions from on-road vehicles in the Kaisermühlen tunnel (Vienna, Austria). Environ Sci Technol 41:4938–4945

Morton O, Puchelt H, Hernández E, Lounejeva E (2001) Traffic-related platinum group elements (PGE) in soils from Mexico City. J Geochem Explor 72:223–227

Morton-Bermea O, Amador-Muñoz O, Martínez-Trejo L, Hernández-Álvarez E, Beramendi-Orosco L, García-Arreola ME (2014) Platinum in $PM_{2.5}$ of the metropolitan area of Mexico City. Environ Geochem Health. doi:10.1007/s10653-014-9613-8

Pan S, Sun Y, Zhang G, Chakraborty P (2013) Spatial distributions and characteristics of platinum group elements (PGEs) in urban dusts from China and India. J Geochem Explor 128:153–157

Pope CA, Burnett RT, Thun MD, Calle EE, Krewski D, Ito K, Thurston GD (2002) Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution. J Am Med Assoc 287:1132–1141

Qi L, Zhou MF, Zhao Z, Hu J, Huang Y (2011) The characteristics of automobile catalyst-derived platinum group elements in road dusts and roadside soils: a case study in the Pearl River Delta region, South China. Environ Earth Sci 64:1683–1692

Rauch S, Lu M, Morrison G (2001) Heterogeneity of platinum group metals in airborne particles. Environ Sci Technol 35:595–599

Rauch S, Peucker-Ehrenbrink B, Molina LT, Molina MJ, Ramos R, Hemond H (2006) Platinumgroup elements in airborne particles in Mexico City. Environ Sci and Technol 40:7554–7560

Spada N, Bozlaker A, Chellam S (2012) Multi-elemental characterization of tunnel and road dusts in Houston, Texas using dynamic reaction cell-quadrupole-inductively coupled plasma–mass spectrometry: evidence for the release of platinum group and anthropogenic metals from motor vehicles. Anal Chim Acta 735:1–8

Wang J, Zhu RH, Shi YZ (2007) Distribution of platinum group elements in road dust in the Beijing metropolitan area, China. J Environ Sci 19:29–34

Zereini F, Alt F, Messerschmidt J, von Bohlen A, Liebl K, Püttmann W (2004) Concentration and distribution of Platinum group elements (Pt, Pd, Rh) in airborne particulate matter in Frankfurt am Main, Germany. Environ Sci Technol 38:1686–1692

Zereini F, Alsenz H, Wiseman CLS, Püttmann W, Reimer E, Schleyer R, Bieber E, Wallasch M (2012) Platinum group elements (Pt, Pd, Rh) in airborne particulate matter in rural vs. urban areas of Germany: concentrations and spatial patterns of distribution. Sci Total Environ 416:261–268

Solubility of Emitted Platinum Group Elements (Pt, Pd and Rh) in Airborne Particulate Matter (PM_{10}) in the Presence of Organic Complexing Agents

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Abstract The purpose of this study was to examine the influence of the common organic complexing agents, L-methionine and ethylenediaminetetraacetic acid (EDTA), on the solubility of the platinum group elements (PGE), platinum (Pt), palladium (Pd) and rhodium (Rh), associated with field-collected airborne PM_{10}. For comparative purposes, the Standard Reference Material 2557 (Used Auto Catalyst Monolith) was also analysed. The concentrations of PGE were determined for both soluble extracts and the filtered insoluble elemental fractions. To minimize matrix effects, samples first underwent a co-precipitation procedure with Te prior to the determination of Pt and Rh. Platinum concentrations were measured using isotope dilution ICP-Q-MS in collision mode with He, while Rh was determined via ICP-Q-MS. For Pd, samples were first co-precipitated with Hg, before concentrations were determined using isotope dilution ICP-Q-MS, also in collision mode with He. The results demonstrate that the presence of the L-methionine, and EDTA increase the solubility of Pt, Pd and Rh present in airborne PM and the SRM 2557. Samples extracted with solutions containing L-methionine had relatively large soluble fractions of 39 % for Pt, 27 % for Pd and 26 % for Rh. Similarly, Pt, Pd and Rh extracted with a solution containing EDTA had an average solubility of 33, 45 and 35 % for these three elements, respectively. The solubility of PGE present in

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the catalytic converter material was much lower, with <4 % for Pt, Pd and Rh. This demonstrates that PGE species present in airborne PM are more soluble compared to that in automotive catalytic converters.

1 Introduction

Numerous studies conducted in Germany, as well as elsewhere, have documented an accumulation of the platinum group elements (PGE), platinum (Pt), palladium (Pd) and rhodium (Rh), in the environment over time, which is directly attributed to their use as catalysts in the control of automotive exhaust emissions (see Zereini et al. 2001, 2004, 2007, 2012a, b; Gómez et al. 2002; Wichmann et al. 2007; Leopold et al. 2008). Several studies which have been undertaken in the Frankfurt am Main region have yielded much information regarding the concentrations, particle size distribution and transport-related spatial patterns of PGE in airborne PM (PM_{10}, $PM_{2.5}$ and PM_1) (Zereini et al. 2012a). Among other things, these studies have demonstrated that the highest concentrations of PGE in airborne PM (PM_{10}) occur in the vicinity of roadways with high volumes of traffic. In a more recent study, Zereini et al. (2012a) reported mean PGE concentrations of 58.5 pg Pd/m^3, 66.7 pg Pt/m^3 and 12.8 pg Rh/m^3 for samples collected in Frankfurt am Main between 2009 and 2010. Similar urban-focused studies, with comparable concentrations of PGE in airborne PM, have been conducted elsewhere, including Japan (Mukai et al. 1990), Rome (Iavicoli et al. 2008), Göteborg (Rauch et al. 2001), Spain (Gomez et al. 2001, 2003), Austria (Kantisar et al. 2003; Limbeck et al. 2007), Buenos Aires (Bocca et al. 2006) and Mexico (Rauch et al. 2006; Morton-Bermea et al. 2014). More recently, airborne PM levels of PGE have also been examined for the US (Hays et al. 2011; Spada et al. 2012; Bozlaker et al. 2014). Overall, these studies provide strong evidence for the presence of elevated concentrations of PGE in the atmosphere on a global scale due to their use as catalysts in the control of harmful vehicular exhaust emissions.

To obtain a better understanding of the potential environmental mobility and bioaccessibility of PGE and their associated health impacts, several experimental studies have been undertaken to determine the solubility of these elements present in various environmental matrices. An earlier study by Alt et al. (1993) determined that ca. 31–43 % of the total emitted Pt present in airborne dust is soluble in a solution of 0.07 mol/L HCl. This same study reported a relatively low solubility of 2.5–6.9 % for Pt present in tunnel dust samples extracted with the same solution. In their engine dynamometer experiments, Artelt et al. (1999) observed that <1 % of the total Pt emitted immediately following engine start-up was soluble in 0.9 % NaCl. In another study, Jarvis et al. (2001) determined that Pd present in road dust was more soluble in water compared to Pt and Rh (e.g. 35 % of Pd vs. 0.48 % of Pt extracted with simulated rain). Nachtigall et al. (1996) reported a low solubility for Pt in deionized water (<0.1 %). In another study, the Pt in tunnel dust samples was determined to be more soluble in deionized water compared to the model substance

Pt-black, with soluble fractions of 3.9 and 0.32 % for the different sample materials, respectively (Lustig et al. 1996).

These studies demonstrate that PGE solubility is likely to be highly variable between the individual elements, as well as for each respective element in different sample media. This is due to a variety of factors including sampling conditions and types (e.g. tailpipe vs. environmental samples, tunnel vs. ambient samples) and the extraction solutions used. Generally, the evidence suggests that PGE in environmental samples tend to have a higher solubility compared to samples which contain these elements in the same chemical form as that used in the original catalytic converter material (e.g. tailpipe and tunnel dust samples). Various substances commonly present in the environment, such as organic complexing agents, are likely to modulate the solubility of PGE post-emission. This is supported by a few studies which have shown that Pt has a higher solubility in the presence of organic compounds such as acetate (Wood et al. 1994; Zimmermann et al. 2003; Wood and Van Middlesworth 2004). As for Pd, less is known but the limited evidence indicates that this element's solubility will also be enhanced in a similar fashion in the presence of certain organic compounds (Wood et al. 1994; Zimmermann et al. 2003).

The goal of this study is to contribute to existing knowledge regarding the environmental behavior and bioaccessibility of Pt, Pd and Rh and the potential modulating effects of commonly present organic complexing agents. In fulfillment of this goal, extraction experiments were conducted on airborne PM_{10} samples collected in Frankfurt am Main, Germany, using L-methionine and EDTA solutions at variable concentrations over two different time periods.

2 Sample Collection and Processing

2.1 Sampling

Airborne PM_{10} samples were collected in 2009 in Frankfurt am Main using a high volume air sampler (Digitel) at the monitoring station of the Hessische Landesamt für Umwelt und Geologie (Hessian Ministry for Environment and Geology) (coordinates: 50°07`28.53`` N; 8°41`30.88`` E). The site is situated at the curb of a four-lane street with a traffic volume of 32,500 vehicles/day and a speed limit of 50 km/h. Samples were collected on cellulose nitrate membrane filters (pore size: 3 µm, filter diameter: 150 mm). Further information regarding sample collection is detailed in Zereini et al. (2012a, b) and Bruder (2011).

2.2 Materials

A total of 24 PM_{10} samples were chosen for the extraction tests with EDTA and L-Methionine solutions. L-methionine, an essential amino acid which is necessary for various biological functions in organisms, including humans. Ethylenediaminetetraacetic acid is a synthetic chelating agent, which is used in a variety of commercial products and industrial applications. It is widely present in the environment due to its extensive use and persistence (Nowack 2002). L-methionine and EDTA are known to strongly complex with metals). For comparative purposes, 11 samples of the SRM 2557 (Used Auto Catalyst Monolith) underwent the same extraction procedures with these solutions. The certified PGE concentrations for this SRM are 1,131 mg Pt/kg, 233.2 mg Pd/kg and 135.1 mg Rh/kg.

2.3 Sample Extraction

Samples were extracted with EDTA and L-methionine at different concentrations (0.01 and 0.1 M) over two different time periods (24 h and 30 days) to assess the influence of extract time and solution concentration on solubility. Together with the SRM, samples collected on filters were individually placed in 250 ml amber, nontransparent, high density polyethylene bottles with 40 ml of the respective organic solutions. Samples were shaken at room temperature at programmed intervals of 30 min shaking, followed by a 60 min break, on a horizontal mixer over the entire reaction period.

At the end of each respective reaction period of 24 h and 30 days, samples were filtered using 0.2 p polypropylene membrane filters (pore size: 0.2 μm) to separate the soluble (<0.2 μm) from the insoluble (>2 μm) fractions. Given the particle size cut-off of the sample filters, ultrafine particles can be expected to be present in the soluble fraction. The sample extraction procedures are more fully detailed in Bruder (2011).

2.4 Analysis

The insoluble fractions (i.e. filter residues) of PM_{10} and SRM samples were digested with 2 ml HNO_3 (69 % (Suprapure)) and 6 ml HCL (37 % (Suprapure)) in a microwave (CEM MarsXpress) at 160 °C (600 W, ramp time 15 min, 15 min holding time). Prior to digestion, samples were spiked with Pt and Pd (95.71 % ^{198}Pt and 97 % ^{105}Pd) (Cambridge Isotope Laboratories, Woburn, MA, USA). The spike concentrations were adjusted in accordance with expected Pt and Pd levels present in the samples. The soluble and digested insoluble fractions of each respective sample were then heated in Teflon dishes with 2 ml HNO_3 (69 %) (Suprapure, Merck) until near dryness. This step, involving sample heating with concentrated HNO_3, was repeated another 2–3 times before samples were transferred to conical tubes and diluted to the 10 ml mark with 0.5 % HNO_3 (Zereini et al. 2012a, b; Bruder 2011).

To minimize matrix effects, samples were first co-precipitated with Te prior to the measurement of Pt and Pd. Rhodium was measured using ICP-Q-MS, while Pt concentrations were determined using isotope dilution and ICP-Q-MS (in collision mode with He) (Gomez et al. 2003; Alsenz et al. 2009). The respective isotopes measured for Rh and Pt were as follows: ^{103}Rh, ^{194}Pt, ^{195}Pt, ^{196}Pt and ^{198}Pt. For Pd, samples underwent a co-precipitation procedure with Hg before concentrations were determined via isotope dilution ICP-Q-MS in collision mode with He (isotopes measured: ^{105}Pd, ^{106}Pd, ^{108}Pd and ^{110}Pd).

Indium (In) and thulium (Tm) were used as internal standards (at 4 µg/L). The ICP-MS settings were as follows: plasma flow 17.7 L/min, auxiliary flow 1.68 L/m, sheath gas flow 0.25 L/min, nebulizer flow 0.94 L/min, ICP RF power 1.40 kW, He gas flow 120 ml/min. The limit of detection, determined as 3 times the standard deviation of the blank, was 4 ng Pd/L, 9 ng Rh/L and 7 ng Pt/L.

The applied method for the determination of PGE, recognized at both a national and international level, has been validated for its reproducibility and accuracy through round robin and comparison tests, as well as through numerous studies using certified reference materials (e.g. BCR 723 (road dust reference material), CANMET CCRMP reference material TDB-1, UMT-1 and WPR-1) (see Gomez et al. 2003; Messerschmidt et al. 2000; Zereini et al. 2004, 2012a, b; Alsenz et al. 2009).

3 Results and Discussion

The results demonstrate that Pt, Pd and Rh associated with airborne PM (PM_{10}), as well as that in the automotive catalyst material (SRM 2557), have an elevated solubility in the presence of the organic complexing agents, EDTA and L-methionine. In the presence of L-methionine, PGE solubility was not found to be significantly different between extract solutions of different strength. The overall mean solubility of Pt was determined to be 39 % for samples (i.e. for both solution concentrations). Intersample variability in Pt solubility was quite high for samples extracted with this complexing agent, ranging between 22 and 55 %. Mean Pd solubility in L-methionine was less with 26 % but variability was also quite high, with a range of 12–53 %. Rhodium was observed to have a similar solubility in L-methionine with 26 % (min–max: 5–66 %) (Table 1).

In contrast to L-methionine solution strength, solubility was observed to vary as a function of extraction period for Pt and Rh, with an increase of 27–42 % for Pt and 20–38 % for Rh after 24 h and 30 days, respectively. However, there was no apparent relationship observed between Pd solubility and extraction time (Table 2). Given the relatively limited number of samples and the intersample heterogeneity observed though, further extraction tests involving more samples would be recommended though to more fully examine the effect of time and extract concentration on solubility.

Table 1 Mean soluble fraction (min–max) (%) of Pt, Pd and Rh in airborne PM (PM_{10}) samples in L-methionine and EDTA solutions (0.01 and 0.1 M and all samples), (n = 12)

	Pt	Pd	Rh
0.01 ML-Met	45.5 (24.4–54.7)	24.4 (12.2–32.1)	30.6 (4.7–66.3)
0.1 ML-Met	28.0 (22.1–33.1)	29.7 (16.7–53.2)	18.7 (7–30.8)
All Samples	39 (22–55)	26 (12–53)	26 (5–66)
0.01 EDTA	40.3 (22.2–67)	21.6 (7.1–51)	15.8 (8–20.4)
0.1 EDTA	27.9 (16.5–33.8)	66.7 (55.3–81.0)	35.5 (7.5–79.8)
All Samples	34 (17–67)	47 (8–81)	26 (8–80)

Table 2 Mean soluble fraction (%) of Pt, Pd and Rh in airborne PM (PM10) samples with L-methionine and EDTA solutions after 24 h and 30 days (0.01 and 0.1 M and all samples, (n = 12)

0.01 ML-Met	Pt	Pd	Rh
1 day	24.4	12.2	22.4
30 days	51.7	27	41.8
0.1 ML-Met			
1 day	28.8	53.2	18.4
30 days	22.1	16.7	30.8
All samples			
1 day	27	33	20
30 days	42	24	38
0.01 EDTA			
1 day	26.3	7.1	19.3
30 days	34	26.3	14.2
0.1 EDTA			
1 day	30.6	55.3	14.3
30 days	29.3	73.4	60.2
All samples			
1 day	29	31	17
30 days	32	50	37

For the extraction tests with EDTA, similar results were observed for PGE. Platinum, Pd and Rh had an overall mean solubility of 34, 47 and 26 % in all samples (0.01 and 0.1 M) EDTA solutions, respectively (Table 1). Intersample variability was observed to be quite high though ranging between 17–67 % for Pt, 8–81 % for Pd and 8–80 % for Rh. An increase in solubility as a function of time for samples extracted with EDTA was observed for all PGE. The solubility increased from 29 to 32 % for Pt, 31 to 50 % for Pd and 17 to 37 % for Rh over the respective time periods of 24 h and 30 days.

Overall, the PGE were observed to display similar trends in their respective solubility in L-methionine and EDTA solutions. A time dependent increase in PGE solubility was also observed for the different extracts used, with the largest soluble fractions measured for the period of 30 days. Only Pd solubility was found to not increase over time in the presence of L-methionine.

At the same time, the intersample solubility for all PGE was observed to be highly variable. This is to be expected, however, as the chemical composition and associated elemental species of airborne PM can vary substantially over time and space as a function of many different site specific factors ranging from the fleet composition on roads to meterological conditions (Zereini et al. 2012a, b). The affinity of elemental species for various organic constituents will be expected to vary accordingly. In contrast to the results for field-collected airborne PM samples, the elemental solubility of the PGE present in the SRM 2557 (Used Auto Catalyst Monolith) samples was observed to be much lower. In the presence of the less concentrated L-methionine solution (0.01 M), Pt, Pd and Rh solubility was relatively low, with means of 3.1 % for Pt (range: 2–6.2 %), 3.4 % for Pd (range: 0.5–7.4 %) and 2.9 % for Rh (range: 1–6.7 %). Similarly, the Pt, Pd and Rh fractions extracted with EDTA were also comparatively small. For instance, the Pt, Pd and Rh in the SRM samples exposed to the 0.01 M EDTA solution had mean soluble fractions of 1.9 % (range: 1–3 %), 6.1 % (range: 2–8.9 %) and 1 % (0.5–1.5 %), respectively (Figs. 1 and 2). The results here are similar to those reported for the same SRM employed in the solubility experiments conducted by Colombo et al. (2008) and Zereini et al. (2012b), which used the simulated lung fluids, artificial lysosomal fluid (ALF) and Gamble's solution. Previous studies have reported a higher solubility for Pt in the presence of organic substances

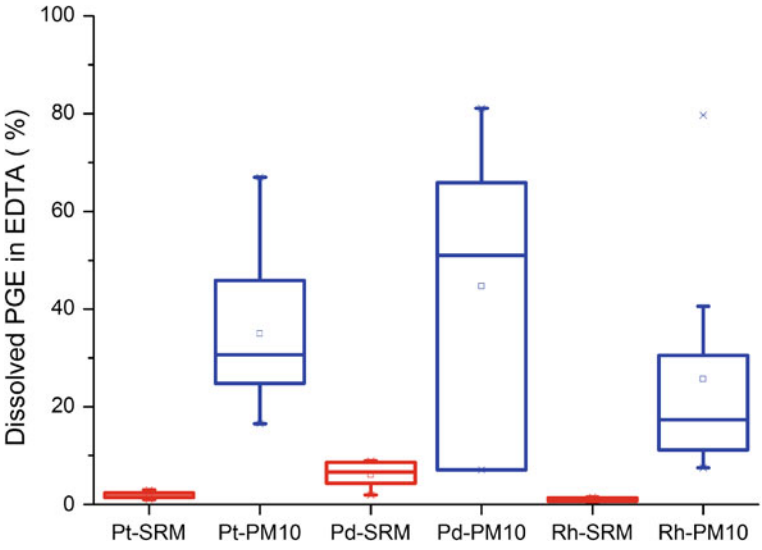

Fig. 1 Solubility (%) of Pt, Pd and Rh in SRM 2557 and airborne PM (PM10) samples in EDTA solutions (0.01 and 0.1 M)

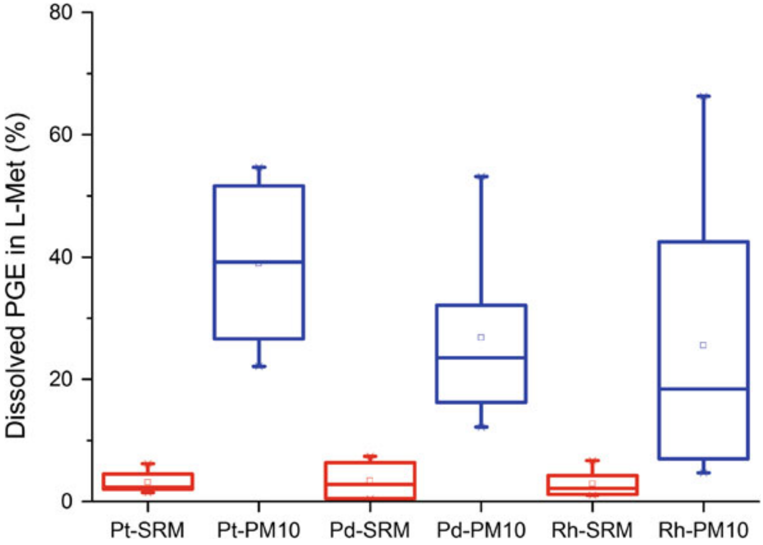

Fig. 2 Solubility (%) of Pt, Pd and Rh in SRM 2557 and airborne PM (PM_{10}) in L-methionine solutions (0.01 and 0.1 M)

(Wood et al. 1994; Zimmermann et al. 2003; Wood and Van Middlesworth 2004). The study here provides additional evidence for the modulating influence of organic complexing agents on the solubility of Pd and Rh.

The total Pd, Pt and Rh concentrations, determined additively from the results for the soluble and insoluble filter fractions for each respective sample, were also observed to be quite variable. The mean concentrations of Pd, Pt and Rh in PM_{10} were 45 pg Pd/m^3 (range: 9–125 pg/m^3), 23 pg Pt/m^3 (range: 7–55 pg/m^3) and 1.6 pg Rh/m^3 (range: 0.6–2.8 pg/m^3). The determined concentrations fall within the same range as those reported for PM_{10} samples collected in Frankfurt am Main over the period of 2008 to 2010 (Zereini et al. 2012a). For this time period, mean concentrations of Pt, Pd and Rh were reported to be 12.4 pg/m^3 (range: 2.0–81 pg/m^3), 43.9 pg/m^3 (1.2–683 pg/m^3) and 3.2 pg/m^3 (range: 0.4–21.3 pg/m^3), respectively.

Using a determined solubility of 47 % for Pd in EDTA solution, we can retrospectively estimate that 21 pg/m^3 of the total level present in PM_{10} occurs in a soluble form on average (of a total concentration of 45 pg/m^3). Similarly, we estimate an average soluble concentration of 5 pg Pt/m^3 and 0.6 pg Rh/m^3 for collected PM_{10} samples. From the results using L-Met, 12 pg Pd/m^3, 5 pg Pt/m^3 and 0.4 pg Rh/m^3 are estimated to be present in a soluble form in PM_{10} samples on average.

The widespread occurrence and accumulation of PGE in the environment on a global basis due to automotive catalytic converter emissions highlights the importance of the study results in contributing to a growing body of knowledge regarding the environmental behavior and the potential hazards of these elements.

The results demonstrated that PGE emitted in roadside environments are likely to be transformed into more soluble species in the presence of organic complexes such as EDTA, upon being deposited on soils or washed into local waterways. This is supported by other studies such as by Zereini et al. (2014), who observed that elemental Pd is easily transformed into a more soluble species in the presence of ligands such as EDTA using Pd-black as the model substance in their experimental studies.

In addition, the results provide evidence that the PGE associated with airborne PM are considerably more soluble compared to that present in the automotive catalytic converter. The PGE embedded in the washcoat of catalytic converters are present in a metallic form (Schlögl et al. 1987; Artelt et al. 1999). This is likely the reason why the PGE in the SRM 2557 have a low solubility in the extracts used here and in other studies (Colombo et al. 2008; Zereini et al. 2012b). Reported that Pt in tunnel dust samples also had a higher solubility when exposed to amino acids in solution compared to Pt-black, where Pt is present in a metallic form similar to that embedded in the wash coat of a catalytic converter. The weight of evidence suggests that the metallic forms of PGE are transformed into more soluble species upon being emitted. This could be due to several factors such as the high temperatures that exist in the exhaust system of vehicles and the chemical composition of the fuel in use. The potential for a post-emission transformation of PGE into more soluble species in the environment is also something in need in of consideration, as we strive to understand the possible behavior and bioaccessibility of these elements.

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References

Alsenz H, Zereini F, Wiseman C, Püttmann W (2009) Analysis of palladium concentrations in airborne particulate matter with reductive co-precipitation, He collision gas, and ID-ICP-Q-MS. Anal Bioanal Chem 395:1919–1927

Alt F, Bambauer A, Hoppstock K, Mergler B, Tölg G (1993) Platinum traces in airborne particulate matter. Determination of whole content, particle size distribution and soluble platinum. Fresenius J Anal Chem 346:693–696

Artelt S, Kock H, König HP, Levsen K, Rosner G (1999) Engine dynamometer experiments: platinum emissions from differently aged three-way catalytic converters. Atmos Environ 33:3559–3567

Bocca B, Caimi S, Smichowski P, Gómez D, Caroli S (2006) Monitoring Pt and Rh in urban aerosols from Buenos Aires, Argentina. Sci Total Environ 358:255–264

Bozlaker A, Spada NJ, Fraser MP, Chellam S (2014) Elemental characterization of $PM_{2.5}$ and PM_{10} emitted from light duty vehicles in the Washburn Tunnel of Houston, Texas: release of Rhodium, Palladium, and Platinum. Environ Sci Technol 48:54–62

Bruder B (2011) Löslichkeit von Platingruppenelementen (Pt, Pd, Rh) und Schwermetallen (As, Cd, Pb, Cr, Ni, Co und Cu) im Luftstaub (PM_{10}, PM2,5 und PM1) in Anwesenheit von organischen Komplexbildnern. Master's Thesis, Goethe Universität Frankfurt am Main, unpublished

Colombo C, Monhemius AJ, Plant JA (2008) Platinum, palladium and rhodium release from vehicle exhaust catalysts and road dust exposed to simulated lung fluids. Ecotoxicol Environ Saf 71:722–730

Gomez MB, Gomez MM, Sanchez JL, Fernandez R, Palacios MA (2001) Platinum and rhodium distribution in airborne particulate matter and road dust. Sci Total Environ 269:131–144

Gómez B, Palacios MA, Gómez M, Sanchez JL, Morrison G, Rauch S, McLeod C, Ma R, Caroli S, Alimonti A, Petrucci F, Bocca B, Schramel B, Zischka M, Petterson C, Wass U (2002) Levels and risk assessment for humans and ecosystems of platinum-group elements in the airborne particles and road dust of some European cities. Sci Total Environ 299:1–19

Gomez MB, Gomez MM, Palacios MA (2003) ICP-MS determination of Pt, Pd and Rh in airborne and road dust after tellurium coprecipitation. J Anal At Spectrom 18:80–83

Hays MD, Cho S-H, Baldauf R, Schauer JJ, Shafer M (2011) Particle size distributions of metal and non-metal elements in an urban near-highway environment. Atmos Environ 45:925–934

Jarvis KE, Parry SJ, Piper JM (2001) Temporal and spatial studies of autocatalyst-derived Platinum, Rhodium, and Palladium and selected vehicle-derived trace elements in the environment. Environ Sci Technol 35:1031–1036

Iavicoli I, Bocca B, Caroli S, Caimi S, Alimonti A, Carelli G, Fontana L (2008) Exposure of Rome city tram drivers to airborne platinum, rhodium, and palladium. J Occup Environ Med 50:1158–1166

Kantisar K, Koellensperger G, Hann S, Limbeck A, Puxbaum H, Stingeder G (2003) Determination of Pt, Pd and Rh by inductively coupled plasma sector field mass spectrometry (ICP-SFMS) in size-classified urban aerosol samples. J Anal At Spectrom 18:239–246

Leopold K, Maier M, Weber S, Schuster M (2008) Long-term study of palladium in road tunnel dust and sewage sludge ash. Environ Pollut 156:341–347

Limbeck A, Puls C, Handler M (2007) Platinum and palladium emissions from on-road vehicles in the Kaisermühlen tunnel (Vienna, Austria). Environ Sci Technol 41:4938–4945

Lustig S, Zang S, Michalke B, Schramel P, Beck W (1996) Transformation behaviour of different platinum compounds in clay-like humic soil: speciation investigations. Sci Total Environ 188:195–204

Messerschmidt J, von Bohlen A, Alt F, Klockenkämper R (2000) Separation and enrichment of palladium and gold in biological and environmental samples, adapted to the determination by total refection X-ray fluorescence. The Analyst 125:397–399

Morton-Bermea O, Amador-Muñoz O, Martínez-Trejo L, Hernández-Álvarez E, Beramendi-Orosco L, García-Arreola ME (2014) Platinum in $PM_{2.5}$ of the metropolitan area of Mexico City. Environ Geochem Health. doi:10.1007/s10653-014-9613-8

Mukai H, Ambe Y, Morita M (1990) Flow injection inductively coupled plasma mass spectrometry for the determination of platinum in airborne particulate matter. J Anal At Spectrom 5:75–80

Nachtigall D, Kock H, Artelt S, Levsen K, Wünsch G, Rühle T, Schlögl R (1996) Platinum solubility of a substance designed as a model for emissions of automobile catalytic converters. Fresenius J Anal Chem 354:742–746

Nowack B (2002) Environmental chemistry of aminopolycarboxylate chelating agents. Environ Sci Technol 36:4009–4016

Rauch S, Lu M, Morrison G (2001) Heterogeneity of platinum group metals in airborne particles. Environ Sci Technol 35:595–599

Rauch S, Ehrenbrink BP, Molina LT, Molina MJ, Ramos R, Hemond HF (2006) Platinum group elements in airborne particles in Mexico City. Environ Sci Technol 40:54–60

Schlögl R, Indlekofer G, Oelhafen P (1987) Mikropartikelemissionen von Verbrennungsmotoren mit Abgasreinigung, Röntgen-Photoelektronenspektroskopie in der Umweltanalytik. Angew Chem 99:312–322

Spada N, Bozlaker A, Chellam S (2012) Multi-elemental characterization of tunnel and road dusts in Houston, Texas using dynamic reaction cell-quadrupole-inductively coupled plasma-mass spectrometry: evidence for the release of platinum group and anthropogenic metals from motor vehicles. Anal Chim Acta 735:1–8

Wichmann H, Anquandah G, Schmidt C, Zachmann D, Bahadir M (2007) Increase of platinum group element concentration in soils and airborne dust in an urban area in German. Environ Sci Technol 388:121–127

Wood S, Tait C, Vlassopoulos D, Janecky D (1994) Solubility and spectroscopic studies of the interactions of palladium with simple carboxylic acids and fulvic acid at low temperature. Geochim Cosmochim Acta 58:625–637

Wood S, Van Middlesworth J (2004) The influence of acetate and oxalate as simple organic ligands on the behaviour of palladium in surface environments. Can Mineral 42:411–421

Zereini F, Alsenz H, Wiseman CLS, Püttmann W, Reimer E, Schleyer R, Bieber E, Wallasch M (2012a) Platinum group elements (Pt, Pd, Rh) in airborne particulate matter in rural vs. urban areas of Germany: concentrations and spatial patterns of distribution. Sci Total Environ 416:261–268

Zereini F, Wiseman CLS, Püttmann W (2012b) In vitro investigations of Platinum, Palladium and Rhodium mobility in urban airborne particulate matter (PM_{10}, $PM_{2.5}$ und PM_1) using simulated lung fluids. Environ Sci Technol 46:10326–10333

Zereini F, Wiseman C, Püttmann W (2007) Changes in palladium, platinum and rhodium concentrations and their spatial distribution in soils along a major highway in Germany from 1994 to 2004. Environ Sci Technol 41:451–456

Zereini F, Alt F, Messerschmidt J, Bohlen A, Liebl K, Püttmann W (2004) Concentration and distribution of platinum group elements (Pt, Pd, Rh) in airborne particulate matter in Frankfurt am Main, Germany. Environ Sci Technol 38:1686–1692

Zereini F, Wiseman C, Alt F, Messerschmidt J, Müller J, Urban H (2001) Platinum and rhodium concentrations in airborne particulate matter in Germany from 1988 to 1998. Environ Sci Technol 35:1996–2000

Zereini F, Wiseman CLS, Vang M, Albers P, Schneider W, Schindl R, Leopold K (2014) Einfluss von organischem Komplexbildner Ethylendiamintetraessigsäure (EDTA) auf die Transformation und Löslickeit von metallischem Palladium (Pd-Mohr) und Palladium(II)oxid (PdO). 14. Edelmetall-Forum, Universität Ulm

Zimmermann S, Menzel CM, Stüben D, Taraschewski H, Sures B (2003) Lipid solubility of the platinum group metals Pt, Pd and Rh in dependence on the presence of complexing agents. Environ Pollut 124:1–5

The Influence of Anionic Species (Cl^-, NO_3^-, SO_4^{2-}) on the Transformation and Solubility of Platinum in Platinum/Aluminum Oxide Model Substance

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Abstract The solubility of Pt in a platinum/aluminum oxide (Pt/Al_2O_3) compound as a function of substrate age (fresh vs. aged) and acid solution pH and anionic species concentration (Cl^-, NO_3^-, SO_4^{2-}) was examined. The results demonstrated that solution pH strongly influenced Pt solubility, with a decrease in elemental solubility observed with increases in pH for all three solutions examined. The presence of Cl^- in solution had a stronger influence on Pt solubility compared to NO_3^- and SO_4^{2-}. Solubility was also dependent on reaction time, with the highest solubility observed for the longer extraction period of 30 days. In addition, Pt solubility was also higher for "fresh" compared to the aged model substance. The examination of surface particle chemistry of the model substrate using x-ray photoelectron spectroscopy (XPS) following treatment with 1 M and 0.1 M HCl showed a transformation in Pt bound to alumina particles. After treatment, XPS confirmed the increased presence of Pt(II) on sample particle surfaces. In contrast, untreated samples consisted primarily of particles with surfaces dominated by Pt(VI). Samples which were filtered under normal atmospheric conditions contained particles with more Pt(II) on particle surfaces compared to samples which were filtered in the presence of N gas. A similar trend was also observed for samples treated with 1 M HCl. The transformation of Pt was also influenced by the presence of O which suggests that Pt can be easily changed into more soluble species under environmental conditions.

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1 Introduction

Platinum group element (PGE) concentrations in the environment have consistently increased since the introduction of automotive catalytic converters to regulate harmful exhaust emissions (Zereini et al. 2007, 2012a; Wichmann et al. 2007; Leopold et al. 2008). The three primary catalysts employed in catalytic converters, namely, platinum (Pt), palladium (Pd) and rhodium (Rh), have been used in various concentrations and combinations over the course of the last three decades. Of the total world production of PGE, 54 % Pt, 84 % Pd and 80 % Rh was consumed by the automotive catalytic converter industry in 2013 (Alison Cowley 2013).

Platinum group elements are released primarily in particulate form in the atmosphere as a result of various mechanical, thermal and chemical stresses (Schlögl et al. 1987). In addition to Pt-containing washcoat particles in the size range of 20–0.1 μm, nanoparticulate Pt- and PtO^{2-}clusters of <5 nm are emitted (Schlögl et al. 1987). The emissions rate of PGE is dependent on vehicle speed, age of catalytic converter and driving behavior (Zereini et al. 2007; Moldovan et al. 2002; Artelt et al. 1999). According to Artelt et al. (2000) about 1 % of the total Pt emitted in automotive exhaust is soluble. In another study, it was demonstrated that ca. 5 % of the Pt present in a model substance containing aluminum oxide particles was soluble (Nachtigall et al. 1996). The same study showed that the presence of chloride ions in an NaCl extraction solution influenced Pt solubility. This supports earlier evidence from Artelt et al. (1999), who reported that ca. 10 % of the Pt in a model substance was soluble in NaCl. The particle size of the model substance used for extraction experiments also appears to be influence Pt solubility, with increases in the soluble fraction with decreases in particle size (Rühle et al. 1997). Further, solubility has been demonstrated to be influenced by the pH, concentration and type of anion species contained in the extraction solution (Zereini et al. 1997; Müller 2011).

In addition to inorganic constituents, the presence of organic complexes can modulate PGE solubility (Lustig et al. 1998; Lustig and Schramel 1999; Zimmermann et al. 2003; Wood and Van Middlesworth 2004; Bruder 2011). More recent experimental studies using physiologically based extraction tests have shown that simulated human lung and gastrointestinal fluids can strongly influence the solubility of PGE derived from automotive catalytic converters (Colombo et al. 2008a, b; Turner and Price 2008; Zereini et al. 2012b).

The solubility of the respective PGE emitted from automotive catalytic converters has also been determined to be highly variable. Alt et al. (1993) reported that 30–43 % of Pt associated with ambient PM was soluble in 0.07 M HCl, compared to 2.5–6.9 % of Pt in street tunnel samples. Palladium in street dust was shown in an earlier study to be more soluble compared to Pt and Rh (Jarvi et al. 2001). Platinum in ambient PM was reported by Zereini et al. (2001) to have a solubility of ca. 10 % in 0.1 M HCl. Bruder (2011) demonstrated that L-methionine and EDTA strongly influenced the solubility of PGE in airborne PM. Of great relevance to the possible impacts of environmental exposures, the solubility of PGE in catalytic converter material has been observed to have a much lower solubility in both simulated biological fluids and in solutions containing organic complexing agents compared to that associated with airborne PM fractions of human health concern (Bruder 2011; Zereini et al. 2012a, b). This provides evidence that the PGE contained in automotive catalytic converters is of a different species compared to that present in airborne PM, which is suggestive of a chemical transformation either during emission and/or release into the environment (Zereini et al. 2012b).

This paper presents new data on the chemical transformation behavior of Pt in Pt/Al_2O_3 model substance in the presence of Cl ions. In addition, results for the influence of pH and the concentration of anionic species (Cl^-, NO_3^-, SO_4^{2-}) on Pt solubility will also be discussed.

2 Sample Material

A Pt on alumina model substance (Pt/Al_2O_3) (Umicore AG & Co. KG) was used for the solubility experiments. The model substance, with a Pt loading of 0.2 % and consisting of Pt-nanoparticles on γ-Al_2O_3, is similar to that used in the washcoat of automotive catalytic converters. Fresh and aged model substance was used for the solubility experiments. To age the material, the model substance was heated at 750 °C for a total of 20 h. At this temperature, the ageing process causes Pt particles to agglomerate, changing the physical composition of the model substance. As such, the model substances will physically behave in a different manner, despite having the same chemical composition. With aging, the color of the model substance changed from white to light grey.

3 Sample Preparation for the X-Ray Photoelectron Spectroscopy (XPS)

Two different solutions of HCl (35 %, Supra grade (ROTH)), 1 and 0.1 M HCl, were used for sample preparation. Approximately 0.5 g of the fresh model substance was added to each respective solution in 10 ml centrifuge tubes. Samples placed in 1 M HCl solution were manually shaken several times a day for 5 days, while samples prepared with 0.1 M HCl were agitated over the course of 24 h.

Half of the samples shaken over each of the respective time periods were filtered under normal atmospheric conditions, while the other half were filtered under N_2 only. The filter residues were placed on sample holders in the sample introduction chamber under controlled vacuum conditions with N_2 prior to measurement via XPS. Under high vacuum, a spot of 650 μm^2 on the respective sample surfaces is measured. As the $4f_{7/2}$-orbital of Pt and the 2p-orbital of Al partially overlap, the 2 s orbital of Al and the $4d_{5/2}$-orbital of Pt was used for correction purposes. Untreated fresh model substance samples, as well as those treated with HCl, were analysed using XPS.

4 Sample Extractions

To determine Pt solubility of the model substance, HNO_3 (Supra 69 %, (ROTH)), HCl (Supra 35 % (ROTH)) and H_2SO_4 (Supra 95 % (ROTH)) were used at different solution strengths to assess the influence of different pH levels (0.3, 1.2, 1.9, 3, 3.8 and 4.2) and concentrations of different anionic species (Cl^-, NO_3^-, SO_4^{2-}): 0.00001, 0.0001, 0.001, 0.01, 0.1 and 1 M. The pH of the acid solutions were measured both before and after filtration with the model substance. Centrifuge tubes were filled to the 10 ml mark with the respective solutions, which were prepared with distilled water. A total of 10.5 ± 0.5 mg was added to each of the sample tubes. Samples were repeatedly shaken on a daily basis over three different extraction periods: 24 h, 5 days and 4 weeks. Following the reaction period, the sample tubes were shaken one last time and filtered under vacuum (filter size: 50 mm, pore size: 0.2 μm). Filtered solutions were transferred to Teflon dishes and evaporated on a heating plate until near dryness. One ml of HNO_3 (69 %) was then added to samples and evaporated again. This step was repeated twice before being diluted to 10 ml with 0.5 % HNO_3 in centrifuge tubes for measurement via ICP-Q-MS (in collision mode with He). As the sample solutions contained high concentrations of Pt and no potential matrix interferences, it was not necessary to isolate and pre-enrich samples prior to measurement, as is the case for environmental samples. The ICP-Q-MS settings were as follows: Plasma flow 17.7 L/min, Auxiliary flow 1.68 L/m, Sheath Gas Flow 0.25 L/min, Nebulizer flow 0.94 L/min, ICP RF power 1.40 kW, He gas flow 120 ml/min.

5 Analysis

Particle surface chemistry was analysed via XPS and the sample material characterized using raster electron microscopy (REM) and transmission electron microscopy (TEM) (analyses performed at AQura GmbH). With REM, the distribution of Pt particles on the γ-Al_2O_3 surface and the size of the alumina particles determined. The size of the Pt particles was determined using TEM. In addition to samples extracted over 24 h and 5 days, untreated model substance samples were examined using XPS, REM and TEM for comparative purposes.

6 Quality Control/Quality Assurance

For the solubility experiments, three parallel solutions of all three acids were prepared for all concentrations and measured via ICP-Q-MS. The acids used were all Supra quality (35 % HCl, 69 % HNO_3, 95 % H_2SO_4). A Pt-ICP standard (Merck) was freshly prepared at concentrations ranging from 0.015 to 25 μg/l Pt to calibrate the ICP-Q-MS. The following Pt-isotopes were measured to determine concentrations:

^{192}Pt, ^{194}Pt, ^{195}Pt, ^{196}Pt and ^{198}Pt. Thulium and indium were used as internal standards. To minimize possible spectral interferences, Pt measurements were undertaken with the ICP-Q-MS in collision mode with He. Acid solutions of 0.01 M were used as blanks. The highest Pt concentrations were determined for HCl blanks with 0.0052 ± 0.0022 µg/L. Levels of Pt were 0.0029 ± 0.0004 µg/L and 0.0020 ± 0.0007 µg/L for HNO_3 and H_2SO_4, respectively.

7 Results and Discussion

7.1 Pt Solubility in Pt/Alumina Model Substance

The solubility of Pt in the model substance was influenced by the concentration of the acid solutions and associated pH levels, with larger soluble Pt fractions measured in concentrated acid solutions (with lower pH levels). The lowest Pt solubility was observed for the weakest acid solutions of 0.00001 M (pH: 4.2 ± 0.2), while samples in the 1 M solutions (pH: 0.3) had the highest solubility.

Platinum had the highest solubility in fresh model substance samples extracted with 1 M HCl for 24 h (mean: 0.575 ± 0.26 % Pt) (Table 1). The lowest solubility was observed for samples leached in 0.0001 M HCl (mean: 0.001 ± 0.0002 %). A similar trend was also observed for aged model substance samples, with a mean solubility of 0.198 ± 0.003 % in 1 M HCl and 0.0008 ± 0.0003 % in 0.00001 HCl. Similarly, Zereini et al. (1997) reported the highest Pt solubility for milled automotive catalyst material extracted in an acidic solution with a pH of 1. The results here support evidence for a low Pt solubility in solutions with a pH of ≥2.

Although both fresh and aged samples were most soluble at the lowest pH levels, there were differences in terms of their respective degree of solubility in the various HCl solutions. Specifically, the Pt in the fresh model substrate was more soluble compared to that in aged samples. For instance, the Pt in the fresh substance was 0.575 ± 0.26 % in 1 M HCl (pH: 0.3), while Pt in aged samples had a mean soluble fraction of 0.198 ± 0.003 % in the same solution (Table 2).

Table 1 Soluble Pt fractions in fresh model substance (Pt/Al_2O_3) treated with three different acid solutions (HCl, HNO_3 and H_2SO_4) at variable molarities

Molarity (M)	Dissolved Pt in HCl (%)	Dissolved Pt in HNO_3 (%)	Dissolved Pt in H_2SO_4 (%)
0.00001	0.001 ± 0.0002	0.0006 ± 0.001	0.001 ± 0.001
0.0001	0.002 ± 0.001	0.0008 ± 0.0001	0.004 ± 0.003
0.001	0.010 ± 0.007	0.011 ± 0.005	0.039 ± 0.009
0.01	0.067 ± 0.041	0.024 ± 0.006	0.159 ± 0.013
0.1	0.403 ± 0.014	0.390 ± 0.234	0.228 ± 0.071
1	0.575 ± 0.26	0.457 ± 0.153	0.279 ± 0.011

Table 2 Soluble Pt fractions in aged model substance (Pt/Al_2O_3) treated with three different acid solutions (HCl, HNO_3 and H_2SO_4) at variable molarities

Molarity (M)	Dissolved Pt in HCl (%)	Dissolved Pt in HNO_3 (%)	Dissolved Pt in H_2SO_4 (%)
0.00001	0.0008 ± 0.0003	0.0006 ± 0.0002	0.0004 ± 0.0001
0.0001	0.0006 ± 0.0003	0.0005 ± 0.0001	0.0006 ± 0.0003
0.001	0.004 ± 0.0001	0.003 ± 0.0004	0.0015 ± 0.001
0.01	0.031 ± 0.0001	0.038 ± 0.002	0.0008 ± 0.0001
0.1	0.115 ± 0.003	0.098 ± 0.003	0.0036 ± 0.0009
1	0.198 ± 0.003	0.137 ± 0.013	0.122 ± 0.024

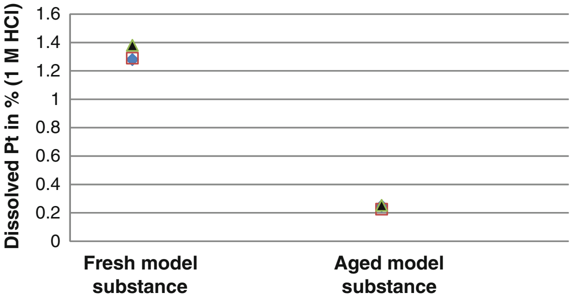

Fig. 1 Soluble Pt fractions (%) measured for fresh and aged model substance extracted with 1 M HCl after 5 days

Similarly, fresh samples extracted over a period of 5 days had a higher solubility compared to aged model substance. With a mean soluble fraction of 1.3 ± 0.1 % in 1 M HCl compared to 0.2 ± 0.01 % (Fig. 1) for the fresh and aged samples, respectively, the former was 5-times more soluble. After a reaction period of 4 weeks, the solubility of Pt in fresh and aged samples increased, with considerably higher rates again measured for fresh model substance, e.g. 2.2 ± 0.9 % versus 0.5 ± 0.1 % in 1 M HCl.

Platinum solubility in 1 M HCl increased over time for both fresh and aged samples (Fig. 2). The concentrations of Pt in fresh model substance increased from 0.575 ± 0.26 after 24 h to over 1.3 ± 0.1 % after 5 days and 2.2 ± 0.9 % after 4 weeks. In aged model substance, Pt solubility increased from 0.198 ± 0.003 % after 24 h to 0.5000 ± 0.1 % after 4 weeks. The highest Pt solubility was observed for fresh samples after 4 weeks with 2.2 ± 0.9 %. The lowest solubility was measured for aged model substance after a 24 h extraction period, with 0.2 ± 0.002 % of the total amount present. In sum, the experimental test demonstrated that the fresh model substance was ca. 3-times more soluble compared to that in the aged model substance. Differences observed in solubility between the fresh and aged model substrate may be attributed to the particle size of the respective samples (Fig. 3).

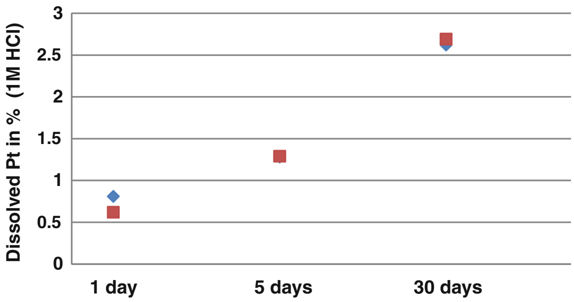

Fig. 2 Time trends in Pt solubility (%) for fresh model substance extracted with 1 M HCl

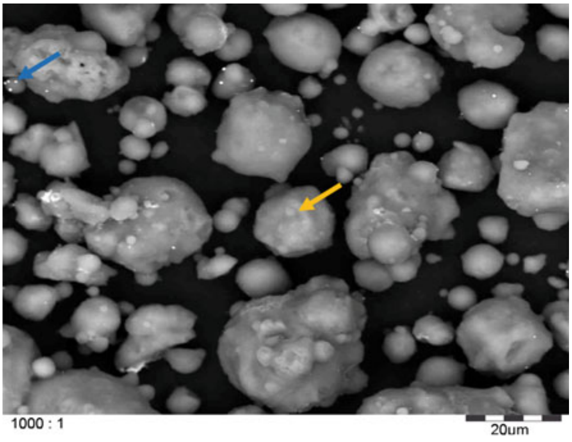

Fig. 3 REM image of the fresh model substance

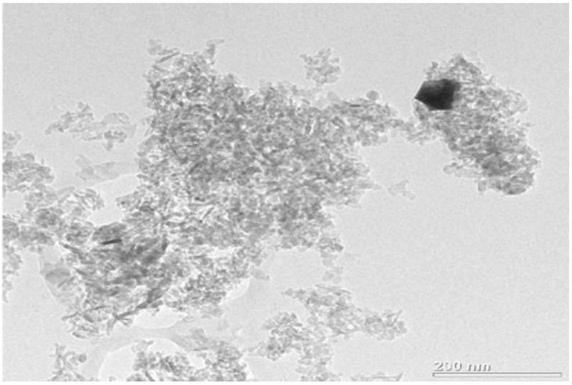

Fig. 4 TEM image of the fresh model substance

The TEM images show that the Pt-nanoparticles are dispersed and strongly bound to the alumina particles of the fresh model substance, which have a diameter ranging from 20 to 150 nm (Fig. 4). The alumina particles of the aged substance have a larger particle surface diameter of 50 to 500 nm, which amounts to a particle surface area 3-times less than that compared to the fresh model substance. Clearly, the aging process led to an agglomeration of alumina particles, thereby effectively reducing their particle surface area and potential for Pt to be mobilized into solution. The results provide an explanation for the observation made in previous studies that Pt emissions are dependent on the age of the automotive catalytic converter, with older catalysts releasing lower levels of Pt compared to new or fresh ones, as already reported in standing motor bench tests from the 1980s (Artelt et al. 1999). In an experimental study by Rühle et al. (1997), the solubility of two model catalyst powders were demonstrated to be dependent on particle size, with increases in Pt mobility with decreases in particle size. Artelt et al. (1999) provided further evidence of the importance of particle size on solubility. As much as 10 % of the Pt in a model catalyst powder was demonstrated to be soluble in NaCl solution.

Platinum solubility in HNO_3 was similar to that for HCl, with solubility being influenced by both age of the model substance and the molarity of the extract solution used (and, with that, pH level). The highest Pt solubility was measured for fresh samples extracted with 1 M, with 0.457 ± 0.153 %. The lowest solubility was determined for samples leached with 0.0001 M (mean: 0.0006 %). Similarly, the Pt solubility of aged model substance samples decreased with decreases in the molarity (and increases in pH) of HNO_3, with fractions of 0.0006 ± 0.0002 and 0.137 ± 0.013 % for 0.00001 and 1 M, respectively. Fresh model substance samples were 3-times more soluble compared to aged samples. Of the 10 mg of model substance used, less than 0.5 % of the fresh and 0.14 % of the aged samples were soluble in 1 M HNO_3. Again, differences in solubility is likely due to the aging process leading to an agglomeration of particles and, as a result, a reduction of the reactivity of particle surfaces.

For H_2SO_4, Pt solubility was observed to be similar to that for HCl and HNO_3. Pt solubility decreased with a reduction in the molarity of H_2SO_4 solutions, with only 0.001 ± 0.001 % of Pt being measured in samples extracted with 0.00001 M. Fresh model substrate had a mean solubility of 0.279 % compared to 0.122 % for fresh samples in 1 M H_2SO_4, confirming observations that aged model substance tended to have a lower solubility.

In comparing Pt solubility in different acid solutions, samples extracted with HCl had the highest soluble fractions, followed by HNO_3 and H_2SO_4. The lowest solubility was observed for H_2SO_4, despite the fact that H^+ ions are present at twice the concentration compared to the other acid solutions. This is suggestive of the important influence of anions (Cl^-, NO_3^-, SO_4^{2-}) in contributing to solubility. The XPS results for Pt samples treated with HCl also support this. Using a synthetic model substance consisting of aluminum oxide particles dispersed with 5 % Pt, Nachtigall et al. (1996) demonstrated that the presence of chloride ions in NaCl enhanced the solubility of Pt. The greater influence of NO_3 on the solubility of Pt compared to SO_4^{2-} observed here may be attributed to the higher oxidizing potential of nitrate ions. Similarly, elemental Pd has also been shown to be less soluble in HNO_3 and H_2SO_4 compared to HCl (Poprizki 2014).

7.2 Particle Surface Chemistry Analysis via XPS

Model substance samples were treated with 1 M and 0.1 M HCl (35 %) over two different time periods to assess the transformation behavior of Pt (i.e. 24 h and 5 days, respectively). Following the respective reaction periods, sample residues were either filtered under normal atmospheric conditions or N_2 only and placed in a transfer chamber for XPS analysis. As the $4f_{7/2}$-orbital of Pt partially overlaps with the 2p-orbital of Al, the $4d_{5/2}$-orbital for Pt and the 2 s-orbital of Al are also considered for the purposes of quantification. In addition to Pt, Al, Cl, C and O on the topmost atomic layers of the Pt-model substance are measured.

Samples treated with 1 M HCl had a substantial reduction in the intensity of the 4d5 orbital for Pt (Table 3). The untreated model substance samples had a measured Pt intensity of 0.48 %. Treated samples filtered under normal atmospheric conditions had an intensity of 0.26 %, which was not that different from those filtered under N_2 (0.23 %). In addition, untreated samples had an Al and O intensity of 41.5 and 55.6 %, respectively. Treated samples filtered under normal atmospheric conditions had measured intensities of 40.7 % Al, 54.9 % O and 1.88 % Cl. Intensities of 48.2 % Al, 45.8 % O and 1.31 % Cl were determined for samples filtered under N_2 only.

High amounts of Pt(IV) (59.2 %) were detected on the surface of untreated model substance particles (i.e. 59.2 %, binding energy of 317.6 eV) (Table 4). In

Table 3 Quantitative XPS spectral results of untreated fresh model substance versus 1 M HCl treated samples (atom-%)

Element	Pt/Al_2O_3 (1 M HCl) filtered in the air (O) (in atom %)	Pt/Al_2O_3 (1 M HCl) filtered in N (in atom %)	Pt/Al_2O_3 fresh model substance (in atom %)
O 1s	54.9	45.8	55.6
Al 2s	40.7	48.2	41.5
C 1s	2.27	4.47	2.45
Cl 2p	1.88	1.13	–
Pt 4d5	0.26	0.23	0.48

Table 4 Results of the Gauss-/Lorentz curve analysis of measured XPS signals of fresh untreated versus 1 M HCl treated model substance samples (binding energy in eV)

Element	Pt/Al_2O_3 (1 M HCl) filtered in the air (O) eV atom %		Pt/Al_2O_3 (1 M HCl) filtered in N eV atom %		Pt/Al_2O_3 fresh model substance eV atom %	
O 1s	530.5 531.4	51.8 48.2	530.2 531.0	49.2 50.8	529.9 531.0	49.9 50.1
Pt 4d5	314.0 316.8 318.5	16.0 43.8 40.2	311.7 315.3 318.2	12.7 43.8 43.5	312.59 315.07 317.6	6.31 34.5 59.2

contrast, larger amounts of Pt(II) were detected on the particle surfaces of treated samples. Samples filtered under normal atmospheric conditions and N_2 had Pt(II) intensities of 43.8 % (binding energies of 316.8 and 315.3 eV under the different conditions, respectively). Samples filtered under ambient conditions contained larger amounts of partially oxidized Pt, while those isolated under N_2 had more reduced species.

In contrast, the intensity of the Pt 4d5 orbital of samples treated with the weaker 0.1 M HCl was not significantly reduced. The intensity of samples filtered under N_2 was not that different from either untreated samples (0.48 %) or those isolated under ambient conditions (0.43 %). Minimal change was also detected post-treatment on the particle surfaces of Al_2O_3 in samples (filtered under both ambient and N_2 conditions). For the untreated samples, Al intensity was 41.5 %, compared to 40.3 and 39.8 % for treated samples filtered under ambient and N_2 conditions, respectively. For O, the measured intensity was 55.6 % for untreated, 56.5 % for treated, air-filtered and 56.2 % for treated N_2 filtered samples (Table 5).

As samples treated with 1 M HCl demonstrated a high Cl content on the particle surfaces, the samples in 0.1 M HCl were extensively washed with distilled water during filtering. This reduced the Cl residues to 0.88 % in samples filtered under ambient conditions and 0.95 % in samples filtered under N_2 (Table 5). Samples isolated under N_2 conditions, as well as untreated model substance samples, contained higher levels of Pt(IV) on particle surfaces, with an intensity of 54.7 % (binding energy: 3177.0 eV) (Table 6). Similar to samples treated with 1 M HCl, those exposed to 0.1 M HCl and filtered under ambient conditions had a greater presence of Pt(II) on particle surfaces (41.9 %, binding energy: 316.8 eV). Also, samples isolated under ambient conditions contained larger amounts of partially oxidized Pt, while reduced Pt species were clearly present in samples filtered under N_2.

The XPS analyses demonstrated that the treatment of model substance with 1 M and 0.1 M HCl can induce a chemical transformation of Pt particle surfaces. Generally, samples contained higher levels of Pt(II) post-treatment, while the Pt in untreated, original samples was primarily in the form of Pt(IV). Samples filtered under ambient conditions had larger amounts of Pt(II) on the particle surfaces, compared to those isolated under N_2. The intensity of the Pt 4d5 orbital was notably

Table 5 Results of the quantitative calculation of XPS spectra of fresh model substance treated with 0.1 M HCl (atom-%)

Element	Pt/Al_2O_3 (0.1 M HCl) filtered in the air (O) (in atom %)	Pt/Al_2O_3 (0.1 M HCl) filtered in N (in atom %)	Pt/Al_2O_3 fresh model substance (in atom %)
O 1s	56.5	56.2	55.6
Al 2s	40.3	39.8	41.5
C 1s	1.82	2.53	2.45
Cl 2p	0.88	0.95	–
Pt 4d5	0.43	0.48	0.48

Table 6 Results of the Gauss-/Lorentz curve analysis of measured XPS signals of untreated and 0.1 M HCl treated fresh model substance (binding energy in eV)

Element	Pt/Al_2O_3 (0.1 M HCl) filtered in the air (O) eV atom %		Pt/Al_2O_3 (0.1 M HCl) filtered in N eV atom %		Pt/Al_2O_3 fresh model substance eV atom %	
O 1s	530.9	64.6	530.9	65.6	529.9	49.9
	531.9	35.4	531.8	34.4	531.0	50.1
Pt 4d5	313.8	19.5	311.8	12.6	312.59	6.31
	316.8	41.9	315.2	32.7	315.07	34.5
	319.4	38.6	317.9	54.7	317.6	59.2

reduced in samples treated with 1 M HCl compared to those exposed to 0.1 M HCl, likely due to the greater presence of Cl ions in the more concentrated solution. The reaction time may have also played a role, with greater increases in the solubility of Pt observed for samples treated with 1 M HCl over 5 days relative to those in 0.1 M HCl for 24 h.

The results demonstrate that the presence of oxygen, in addition to Cl ions, can contribute to the transformation of Pt into species which more soluble. Specifically, the results suggest that emitted Pt from catalytic converters may easily be transformed into more soluble species under normal environmental conditions.

References

Alison Cowley (2013) Platinum 2013, Interim review. Johnson Matthey, pp 1–36

Alt F, Bambauer A, Hoppstock K, Mergler B, Tölg G (1993) Platinum traces in airborne particulate matter: Determination of whole content, particle size distribution and soluble platinum. Fresenius J Anal Chem 346:693–696

Artelt S, Kock H, Konig HP, Levsen K, Rosner G (1999) Engine dynamometer experiments: platinum emissions from differently aged three-way catalytic converters. Atmos Environ 33:3359–3567

Artelt S, Levsen K, König HP, Rosner G (2000) Engine test bench experiments to detrermine platinum emissions from three-way catalytic converters. In: Zereini F, Alt F (eds) Anthropogenic platinum group element emissions. Springer, Berlin, New York, London, pp 33–44

Bruder B (2011) Löslichkeit von Platingruppenelementen (Pt, Pd, Rh) und Schwermetallen (As, Cd, Pb, Cr, Ni, Co und Cu) im Luftstaub (PM_{10}, PM2,5 und PM1) in Anwesenheit von organischen Komplexbildnern. Master's Thesis, Goethe Universität Frankfurt am Main (unpublished)

Colombo C, Monhemius AJ, Plant JA (2008a) Platinum, palladium and rhodium release from vehicle exhaust catalysts and road dust exposed to simulated lung fluids. Ecotox Environ Safety 71:722–730

Colombo C, Monhemius AJ, Plant JA (2008b) The estimation of the bioavailabilities of platinum, palladium and rhodium in vehicle exhaust catalysts and road dust using a physiological based extraction test. Sci Total Environ 389:46–51

Jarvi K, Parry S, Piper M (2001) Temporal and spatial studies of autocatalyst-derived platinum, rhodium and palladium and selected verhicle-derived trace elements in the environment. Environ Sci Technol 35:1031–1036

Leopold K, Maier M, Weber S, Schuster M (2008) Long-term study of palladium in road tunnel dust and sewage sludge ash. Environ Pollut 156:341–347

Lustig S, Zang S, Beck W, Schramel P (1998) Dissolution of metallic platinum as water soluble species by naturally occurring complexing agents. Mikrochim Acta 129:189–194

Lustig S, Schramel P (1999) Zum Transformationsverhalten Kfz-emittierten Platins in einem Boden und Platinaufnahme durch Pflanzen. In: Zereini F, Alt F (eds) Emissionen von Platinmetallen. Springer, Berlin, pp 239–247

Moldovan M, Rauch S, Morrison G, Gomez M, Palacios MA (2002) Impact of ageing on platinum group elements and contaminants in automobile catalysts. Environ Sci Technol 196:199–208

Müller I (2011) Löslichkeit und Oberflächeneigenschaft von Platin in einer Platin/Aluminiumoxid Modellsubstanz – Einfluss des pH-Wertes und der Konzentration der Anionen Spezies (NO_3^-, SO_4^{2-}, Cl^-). Master's Thesis, Goethe-Universität Frankfurt am Main (unpublished)

Nachtigall D, Kock H, Artelt S, Levsen K (1996) Platinum solubility of a substance designed as a model of emissions of automobile catalytic converters. Fresenius J Anal Chem 354:742–746

Poprizki J (2014) Experimentelle Untersuchungen zum Einfluss von anorganischen Anionen (Cl-, NO_3^-, SO_4^{2-},PO_4^{3-}) auf das Transformationsverhalten und die Mobilität von metallischem Palladium (Pd). Master's Thesis, Goethe-Universität Frankfurt am Main (unpublished)

Rühle T, Schneider H, Find J, Herein D, Pfänder N, Wild U, Schlögl R, Nachtigall D, Artelt S, Heinrich U (1997) Preparation and characterization of Pt/Al_2O_3 aerosol precursors as model Pt-emissions from catalytic converters. Appl Catal B 14:69–84

Schlögl R, Indlekofer G, Oelhafen P (1987) Mikropartikelemissionen von Verbrennungsmotoren mit Abgasreinigung, Röntgen-Photoelektronenspektroskopie in der Umweltanalytik. Angew Chem 99:312–322

Turner A, Price S (2008) Bioaccessibility of platinum group elements in automotive catalytic converter particulates. Environ Sci Technol 42:9443–9448

Wichmann H, Anquandah G, Schmidt C, Zachmann D, Bahadir M (2007) Increase of platinum group element concentration in soils and airborne dust in an urban area in German. Environ Sci Technol 388:121–127

Wood S, Van Middlesworth J (2004) The influence of acetate and oxalate as simple organic ligands on the behaviour of palladium in surface environments. Can Mineral 42:411–421

Zereini F, Skerstupp B, Alt F, Helmers E, Urban H (1997) Geochemical behaviour of platinum-group elements (PGE) in particulate emissions by automobile exhausts catalysts: experimental results and environmental investigations. Sci Total Environ 206:137–146

Zereini F, Wiseman C, Alt F, Messerschmidt J, Müller J, Urban H (2001) Platinum and rhodium concentrations in airborne particulate matter in Germany from 1988 to 1998. Environ Sci Technol 35:1996–2000

Zereini F, Wiseman CLS, Püttmann W (2007) Changes in palladium, platinum and rhodium concentrations and their spatial distribution in soils along a major highway in Germany from 1994 to 2004. Environ Sci Technol 41:451–456

Zereini F, Alsenz H, Wiseman CLS, Püttmann W, Reimer E, Schleyer R, Bieber E, Wallasch M (2012a) Platinum group elements (Pt, Pd, Rh) in airborne particulate matter in rural vs. urban areas of Germany: concentrations and spatial patterns of distribution. Sci Total Environ 416:261–268

Zereini F, Wiseman CLS, Püttmann W (2012b) In vitro investigations of platinum, palladium and rhodium mobility in urban airborne particulate matter (PM_{10}, $PM_{2.5}$ und PM_1) using simulated lung fluids. Environ Sci Technol 46:10326–10333

Zimmermann S, Menzel C, Stüben D, Taraschewski H, Sures B (2003) Lipid solubility of the platinum group metals Pt, Pd, and Rh in dependence on the presence of complexing agents. Environ Pollut 124:1–5

Solid State Platinum Speciation from X-ray Absorption Spectroscopic Studies of Fresh and Road Aged Three Way and Diesel Vehicle Emission Control Catalysts

Timothy I. Hyde and Gopinathan Sankar

Abstract The localised Pt environments present in a variety of unused (fresh) and used (road aged) gasoline Three Way (TWC) and Light and Heavy Duty Diesel vehicle emission catalysts (VEC) from both European and North American origins were determined by platinum L3 and L2 edge X-ray absorption spectroscopy (XAS). Detailed laboratory based characterisation was also utilised to support the XAS studies. It was found that it is not sufficient to use the analysis of X-ray absorption near edge structure (XANES) alone to determine the nature of Pt species present in multi component VEC's. Detailed analysis of the Extended X-ray Absorption Fine Structure (EXAFS) at the Pt L3 and L2 edges was therefore extensively utilised and revealed the presence of mainly oxidic species in the fresh catalysts while metallic and bimetallic components were found to be the dominant species in the respective road aged catalysts. More importantly, supporting Cl K-edge X-ray absorption spectroscopy confirmed the absence of chlorine associated with platinum. Hence we dismiss the presence of environmentally significant quantities of chloroplatinate species in VEC's based on weight-of-evidence arguments from chemical analysis, Cl K-edge XANES and analysis of Pt L3 and L2 edge EXAFS data.

1 Introduction

Platinum group metals (PGMs) based catalysts play a crucial role in Vehicle Emission Control (VEC) catalysts to efficiently convert carbon monoxide, oxides of nitrogen (NO_x) and hydrocarbons (Twigg) to more benign gaseous species.

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In addition they are widely used for other catalytic process involving organic transformations (Twigg). VEC catalysts have been studied extensively with the aim to further modify or develop new systems to keep pace with requirements for ever more stringent emission control regulation (Twigg 2006). VEC systems are diverse and complex but generally contain small amounts of highly dispersed PGM in the range of 0.1–1wt% supported on functional and thermally stable structural materials (Twigg; Burch et al. 2002; Rauch et al. 2005) Each of the main converter components (catalytic coating, substrate, mounting materials) has gone through a continuous evolution and redesign process in order to improve the overall performance of the converter while maintaining a competitive cost effectiveness of the complete assembly. Historically most formulations for VEC's included platinum as the active component which has now mostly been replaced by the use of palladium (with rhodium) for most gasoline engines, whilst platinum is required for many current diesel systems. Catalyst-equipped cars were first introduced in the USA in 1974 but only appeared on European roads in 1985. Compulsory use in Europe for petrol engines was brought about by legislation from 1993. It is estimated that the average family car in the US would emit 15 tons of toxic and harmful polluting gases (carbon monoxide, hydrocarbons and nitrogen oxides), over a 10-year life without catalytic control (Catalytic Converters 2014). Increasingly worldwide ever stringent legislation has forced their use not only on passenger cars but now catalytic converters and filters are also fitted to heavy-duty vehicles, motorcycles and non-road engines and vehicles (Working in Partnership for Cleaner Air 2014). Global light duty vehicle sales in 2012 reached 80.9 million (Leggett 2013) and it is estimated that over 85 % of all new cars produced worldwide are equipped with VEC catalysts. Hence usage of PGMs for these applications is considerable. Based on the data from Johnson Matthey, the PGM use in automotive catalysts in 2012 was: Platinum: 3.24 million oz. (40 % of global Pt demand), Palladium: 6.62 million oz. (67 % of global demand) and Rhodium: 7,82,000 oz. (Platinum 2013).

While numerous studies have been carried out in determining the active species present in Three Way Catalyst (TWC) and Diesel Light Duty (LDD) and Heavy Duty (HDD) VECs prior, during and after use (Kaspar and Fornasiero 2003; Kaspar et al. 2003; Prichard and Fisher 2012; Roy and Baiker 2009; Twigg 2011a, b; Twigg and Phillips 2009), still the nature of species present in these systems are not completely understood. More recently (Gomez et al. 2002; Moldovan et al. 1999; Moldovan et al. 2002; Moldovan et al. 2003; Palacios et al. 2000; Sen 2013), there have been concerns about the bioavailability of anthropogenic platinum compounds and chloroplatinate species in particular, in road aged VEC catalysts when used in specific environments. Thus it is our aim to use advanced characterisation methods to determine the types of species present in the road aged VEC catalysts, and in particular any minor components within the overall Pt atomic environments. As formulations differ to reflect varying local emissions standards, road aged VECs were sourced from several locations worldwide for this study.

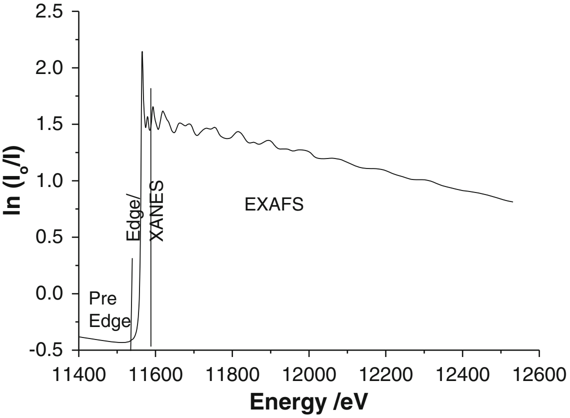
2 Characterisation Methods

Characterisation of VEC catalysts has been carried out by a large number of researchers using a variety of techniques. In particular electron microscopy to determine the particle size and shape of the supported catalysts, Fourier transform Infra Red (FTIR) studies to investigate the nature by adsorbing gaseous molecules such as carbon monoxide, X-ray photoelectron spectroscopy to determine the oxidation states of outer layer atoms, XRD to examine the crystallinity and particle size and X-ray absorption spectroscopy to determine the electronic and geometric structure of the active species (Ezekoye et al. 2011; Rogemond et al. 1999; Levy et al. 1998; Kaneeda et al. 2009; Nagai et al. 2008; Dent et al. 2005; Burch et al. 2002; Sa et al. 2010; Newton and van Beek 2010). Among these techniques X-ray absorption spectroscopy is particularly useful (Koningsberger and Prins 1988), since the measurement can be conducted directly (without high vacuum), with a high degree of sensitivity to determine the structure of a specific atom present in the catalyst by utilising the atom specificity of the technique. There are a number of reviews published in the literature on the use of this technique to study to a range of systems that includes catalysts, to determine precisely the local structure that may be correlated with properties (Aksenov et al. 2006; Bare and Ressler 2009; Feldmann et al. 2009; Graefe et al. 2014; Henderson et al. 2014; Li et al. 2010). Here we demonstrate the use of X-ray absorption spectroscopy (XAS), in particular X-ray absorption near edge structure (XANES) and Extended X-ray absorption fine structure (EXAFS) to determine the types of species present in fresh and road aged VEC catalysts that contain platinum as a major active constituent. In addition the aim of the work is to evaluate the use different approaches within the analysis of the XAS data in the determination of species present in the VEC catalyst. We utilized XAS techniques and show the structure of fresh and road-aged (driven >50,000 km) catalysts employed both in diesel and gasoline engines to demonstrate its power in determining species present in a real catalytic materials. We show selected examples from both these types of systems in addition to model catalysts and the details of the actual catalytic systems are provided in the following references (Ash et al. 2014; Hyde et al. 2011).

2.1 X-ray Absorption Spectroscopy, XAS

Typical X-ray absorption spectrum (XAS) of a platinum foil is shown in Fig. 1. The spectrum consists of three parts, (a) below the absorption edge which is normally termed as pre-edge, (b) absorption edge or X-ray absorption near edge structure (XANES) and (c) extended X-ray absorption fine structure (EXAFS), which are marked in Fig. 1. Typical data collection to obtain XAS spectrum is from transmission mode, in which the sample either in a form of a pellet or compact powder or foil (in the case of pure metal) is placed between two ion chambers, with the first

Fig. 1 Typical X-ray absorption spectrum, showing various regions that can be used for a range of analysis to extract speciation present in a given system. Here Pt L3 edge of Pt metal foil data is shown as an example



ion chamber measuring the incident beam (I_o) and the second one measuring the transmission beam (I_t). In the case of dilute samples where the concentrations of the metal ion of interest is below 1 wt%, the data is collected in a fluorescence mode The absorption coefficient is determined by taking the logarithmic ratio of incident over transmitted beam (ln (I_o/I_t) for a transmission experiment and I_f/I_o for a fluorescence experiment). The majority of the real VEC catalysts contain metal concentrations of below 1 wt% and the data described here were measured using fluorescence mode. The theories behind the EXAFS are well described in many reviews (Aksenov et al. 2006; Russell and Rose 2004) and therefore will not be dealt in detail here. However, it is important to point out that the technique is (a) atom specific since each element has unique absorption edge (b) does not depend on long-range order, therefore any type material (liquid or solid) can be investigated and (c) it does not depend on concentration of the metal—low concentrations in the ppm level can be readily studied. Therefore, XAS is an ideal technique to investigate the type of catalytic systems described in this article. However, while it is highly advantageous to use this method, it is important to realize that there are few disadvantages, in particular an average electronic and geometric structural information is obtained which needs to be carefully interpreted on real systems.

XAS data consists of three regions and among them XANES and EXAFS are the most useful in obtaining chemical information. XANES is sensitive to the oxidation state, local coordination geometry and the nature of ligands present in the first coordination sphere. Although attempts have been made theoretically to understand the XANES spectra of a variety of systems, it is commonly analysed by comparing several model compounds with the materials of interest to draw conclusions on the oxidation state and coordination environment (Fernandez-Garcia 2002; Thomas and Sankar 2001a, b). In addition, more recently, XANES is also used to determine various components (chemical species) present in an unknown system through the use of linear combination fitting methods (LCF) (Graefe et al. 2014; Manceau et al. 2012). While many successful analyses have been done using LCF analysis of unknown systems, use of ill-chosen model compounds can yield misleading results and therefore extra care is necessary in the interpretation of analysis of XANES data using this method. On the other hand, analysis of EXAFS data is much more robust, as the analysis does not depend on the use of model systems. However, it is necessary to guess local structures not too far from reality to gain the best match between experimental and calculated data through least-square refinement procedures and attempts should be made with various possible near neighbours to obtain the best description of the system using this technique. Furthermore, caution should be exercised on the number of independent parameters that are used in the analysis as it will depend on the available data.

For EXAFS data analysis it was sufficient to analyse only the first type of neighbours, up to *ca*. 3 Å, to determine the nature of environment around platinum in the VEC systems. A combined refinement method approach was utilised to analyse the data from all the possible edges of a given sample and simultaneously refined to obtain a unique best fit between experimental and calculated values. For example, in DOC samples, Pt L3, L2 and Pd K-edge data were taken together and analysed simultaneously (Ash et al. 2014). Similarly, for TWC samples, Pt L3 and L2 edges were taken together. In this combined refinement method all the metal-metal bond distances of specific atom-pairs were constrained to be the same and similarly the Debye-Waller factors of similar metal-metal distances were constrained to be identical. Amplitude factors for respective edges were determined from the metal foil data and were fixed for subsequent analysis. As described below it is necessary to study both reference and model catalyst compounds in order to analyse in detail complex catalyst systems such as VEC's.

3 Reference Compounds

In Fig. 2, we show Pt L_3 XANES data of typical model compounds, in particular Pt foil, PtO_2, K_2PtCl_4, representing the three different types of neighbours one would expect in a real catalyst, as they are likely to be prepared using platinum chloride salt as the Pt source through impregnation or other procedures and subsequently they are calcined (in air) to produce the starting catalytic material. The main absorption peak (usually called "white line intensity") is related to the $2p_{3/2}$ to 5d transition (which is the dipole allowed transition). The intensity of the XANES depends on the transition probability and density of unoccupied states (Koningsberger and Prins 1988). Here all the transition states are the same and it is easy to approximate the white line intensity to the density of unoccupied states(Russell and Rose 2004). Hence, Pt^{4+} in the form of PtO_2 shows the maximum intensity and Pt metal foil the least. There are other factors, in particular near neighbour distances (level of bonding contribution), solid state effects and more importantly particle size (nano and bulk) and any bimetallic nature of the material as they can also affect this intensity, perturb the width (shape) and other features (Lei et al. 2011); oxidic compounds show higher intensity compared to, for example, chlorinated compounds. By comparing representative model compounds it is possible to obtain

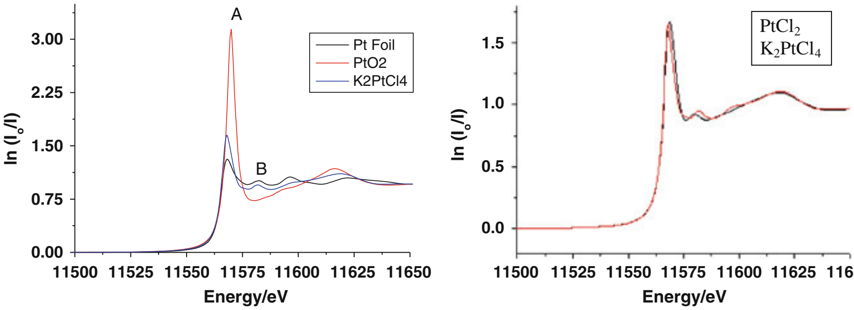


Fig. 2 Pt L_3 edge XANES spectra of model compounds in different oxidation states and in various coordination environments (*left*), and two chlorine containing model compounds (on the *right*)

qualitative information by analysing the XANES data. More recently, several features in the XANES, in particular just above the white line, have been interpreted based on both theory and comparison with the experiments, and used for suggesting possible Pt-X (X first neighbour ligands) species present in a given system (Bare and Ressler 2009). For example, feature B (see Fig. 2 (left)) has been identified as a representative of Cl neighbours in the system (Chen et al. 2009; Ankudinov et al. 2001; Ankudinov et al. 2000; Ankudinov et al. 1998). However, we find firstly this feature is present, although at a different energy, in pure metallic platinum but is absent in model oxidic compounds. In addition, when we compared two different Pt-Cl containing compounds (see Fig. 2 (right)), although both have a similar feature B, they appear to be present at different energies. Therefore, with the current understanding of the spectral features it is not possible to use such qualitative observation to propose the types of species present from the analysis of the XANES data.

In order to determine whether such differences in energy position of the feature B is related to Pt-Cl distance, we carried out curve fitting analysis of the EXAFS data of the Pt-Cl containing reference compounds. To extract non-structural parameters associated with curve-fitting analysis, in particular the amplitude reduction factor (referred commonly as SO_2), we first analysed Pt foil data for which the crystal structure is precisely known. The best fit between experimental and calculated Fourier transforms of the EXAFS data are shown in Fig. 3. Once the amplitude reduction factor is obtained, a further test was carried out using PtO_2 data (once again the crystallographic parameters for PtO_2 are well established) and the best fit between experimental and computed (only first Pt-O shell was considered here) data are shown in Fig. 3. Subsequently, EXAFS of the three Pt-Cl containing compounds were analysed in detail, the best fit to the Fourier transforms of the experimental EXAFS data, and the associated Fourier transforms (FT) are shown in Fig. 3. All the coordination numbers (N), bond distances (R) and Debye-Waller factors (σ^2) derived from the analysis are given in Table 1. From Table 1, it is clear that, in particular Pt-Cl distances are closely similar (well within the typical error

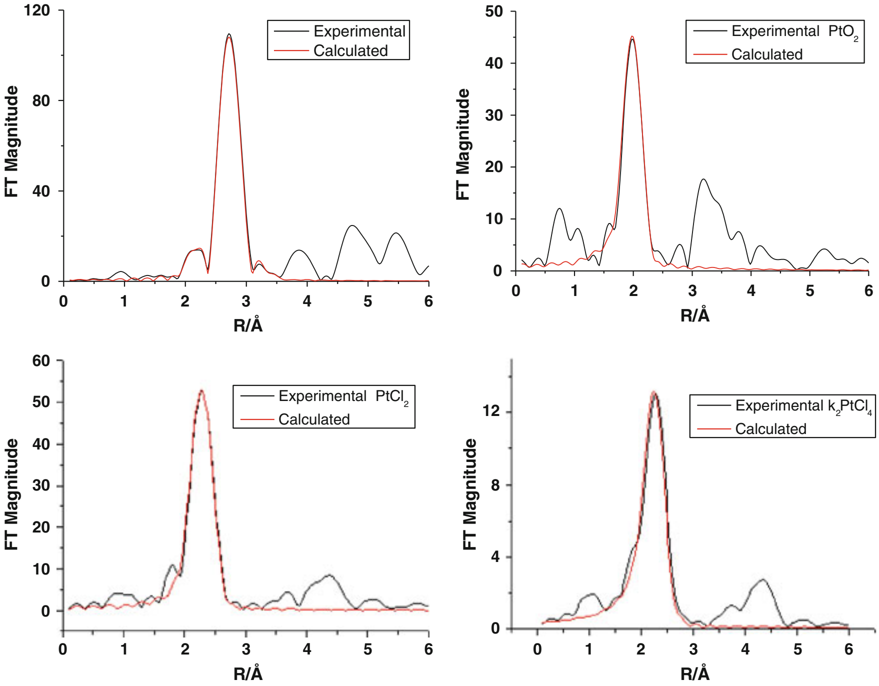


Fig. 3 Fourier transforms of the experimental and calculated EXAFS data for Pt foil (*top left*), PtO_2 (*top right*), $PtCl_2$ (*bottom left*) and K_2PtCl_4 (*bottom right*). Note that in the analysis of Pt foil data, crystal structure data is used to maintain the coordination number of 12 for the first shell and the amplitude reduction factor (0.94) was determined. For other compounds the obtained amplitude reduction factor was kept constant and varied the coordination number. In all the cases the inter-atomic distances were refined along with the E_o and Debye-Waller factor to obtain the best fit

Table 1 Structural parameters of model compounds determined from the analysis of EXAFS data

System	Atom-pair	Coordination number N	Interatomic distance/R (Å)	Debye Waller factor σ^2 (Å^2)	Fit index
Pt foil	Pt-Pt	12	2.77	0.005	36
PtO_2	Pt-O	5.6	2.00	0.0034	39
$PtCl_2$	Pt-Cl	4	2.32	0.0034	31
K_2PtCl_4	Pt-Cl	4.3	2.32	0.0041	32

limits of *ca* ± 0.02 Å, in determining the bond distances from EXAFS) suggesting that the differences in feature B seen for various platinum compounds containing Pt-Cl species may not be related to Pt-Cl distances; further detailed studies are required to substantiate this finding.

4 Model Catalysts

To establish the analysis procedures to determine the types of species present in VEC monolith catalyst, we performed a series of experiments on a standard platinum supported alumina catalysts, 1 % Pt/Alumina, which are denoted as RM1. In Fig. 4 we show the XANES spectra of RM1 catalysts heated in air at different temperatures. It is clear from the XANES spectra that intensity of the white line is higher for the systems processed at low temperatures, compared to Pt foil and lower than that of PtO_2, which indicates that there is more than one component present in these low temperatures systems.

In order to establish the species present in the RM1 catalysts we analysed both the XANES and EXAFS data in detail; LCF method was used for the analysis of the XANES data by taking model compounds shown in Fig. 2. In Fig. 4, we show the XANES data of the three model catalysts activated in air at various temperatures and Fig. 4 (right) we show the variation in white line intensity as well as the phase fraction of PtO_2 and Pt metal phase present in the system estimated from LCF analysis. In Fig. 5, we show the Fourier Transform of the best fit between experimental and calculated data for all the RM1 catalysts and the results of the analysis are given in Table 2. In addition the phase fraction of "PtO" phase with respect to Pt metal phase estimated from the determined coordination number for the Pt–O correlation is plotted in Fig. 4 along with the data estimated from XANES. It is clear from the analysis that RM1—as received sample has significant oxidic component and addition or inclusion of other species in the fitting procedure, in particular Cl neighbours did not yield a better fit to the experimental data or produced physically meaningful results.

RM1 heated at 600 °C for 18 h shows predominantly metallic platinum. However, it was necessary to include an additional Pt–O contribution which resulted in a

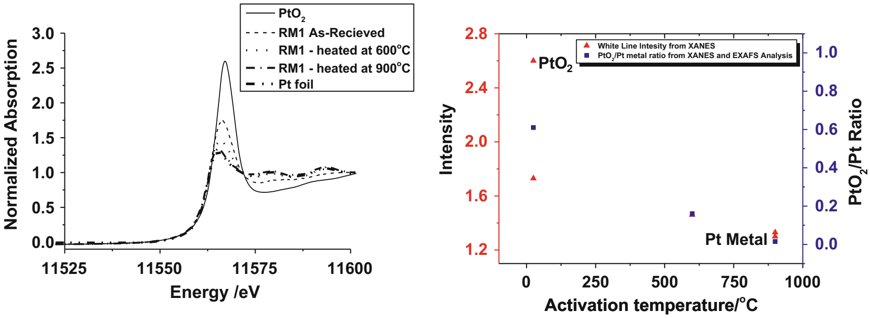


Fig. 4 Comparison of the Pt L_3 XANES of RM1 model Pt/Al_2O_3 catalysts heated in air at different temperatures. On the *right* we show the intensity of the main absorption peak after various heat treatments (given in the x-axis) and in addition we also plot in the same graph the ratio of phases (PtO_2 and Pt metal) present in the system determined through LCF analysis of the XANES data

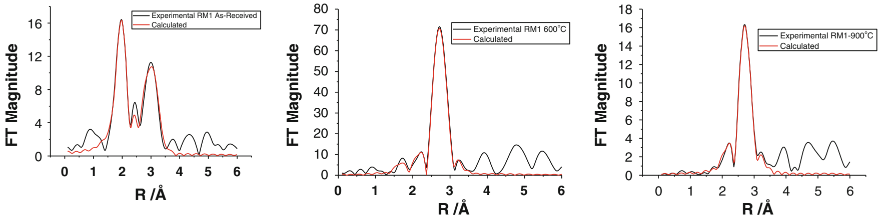


Fig. 5 Fourier transforms of the best fit between experimental and computed EXAFS of model Pt/Al_2O_3 catalysts (RM1) heated in air at different temperatures. RM1 as received (*left*), RM1 heated at 600 °C (*middle*) and RM1 heated at 900 °C (*right*) are shown here

Table 2 Structural parameters obtained from the analysis of EXAFS data of RM1 catalysts as received and calcined at various temperatures

System	Atom-pair	Coordination number N	Interatomic distance/R (Å)	Debye Waller factor σ^2 (Å^2)	Fit index
RM1 as received	Pt-O	2.3	2.01	0.0055	36
	Pt-Pt	3.0	2.75	0.008	
RM1 600 °C	Pt-O	1.0	1.98	0.011	37
	Pt-Pt	9.2	2.76	0.005	
RM1 900 °C	Pt-Pt	11.6	2.76	0.0045	39

better fit with a significant improvement (at the 10 % level) in the R-factor. This suggests that all the oxidic platinum species is not completely converted to metallic platinum when heated at 600 °C. Samples heated at 900 °C could be modelled based only on bulk platinum and there was no need to have additional species to model this data.

5 Diesel VEC Catalysts from EU Sources

The list of samples reported here are given in Table 3 along with typical concentrations of the elements (mainly PGM) are also listed here.

Comparison of the Pt L_3 XANES of Fresh and road aged catalysts, both obtained from their use in a non-coastal environment, along with Pt foil, PtO_2 and K_2PtCl_4 are shown in Fig. 5. Overall observation of the XANES data suggest that fresh catalysts are different from the road aged catalyst with the white line intensity slightly higher for the fresh catalyst compared to the used one. XANES spectra of road aged catalysts are closer to that of bulk metal compared to the fresh catalysts. In general it is found that (a) the road aged catalyst resembles bulk Pt metal more than any other system; (b) a tiny peak appearing above the white line intensity

Table 3 Fresh and Aged catalyst samples and nomenclature utilised in this study selected from EU and USA regions to represent our study. Selected elemental analysis of individual catalysts are also given

Catalyst name	Ageing, region	Vehicle first registered, odometer reading (km)	Chloride (ppm)	Pt (ppm)	Pd (ppm)	Rh (ppm)
TWC						
TWC fresh	NA	–	24	800	30	120
TWC AC	NA road aged, coastal.	2004, 138,500	10	700	25	110
TWC ANC	NA road aged, non-coastal.	2003, 63,000	13	700	<5	150
DOC						
Non-coastal fresh	EU	–	18	8800	4600	17
Non-coastal aged	EU	2007, 56,000	16	8300	3600	<10
Coastal fresh	EU	–	20	3400	<20	<20
Coastal aged	EU	2007, 75,500	17	3400	<20	<20
LDD fresh	NA	–	17	2600	690	<5
LDD AC	NA road aged, coastal		19	2600	560	<5
HDD fresh	NA	–	<10	1800	<5	<5
HDD ANC	NA road aged, non-coastal		22	1800	80	<5
Alumina reference			35			

TWC three way catalyst, *LDD* light duty diesel and *HDD* heavy duty diesel, Location, *EU* European Union, *NA* North America

around 11,585 eV is present in Pt metal foil and is more pronounced in aged catalysts than the starting material. This feature is also present in K_2PtCl_4 and $PtCl_2$, but seems to appear at different energies.

In order to obtain more quantitative information, we carried out a linear combination fit analysis, available in the ATHENA software, on the fresh and road aged catalysts. A typical best fit obtained using a linear combination of Pt foil, PtO_2 and

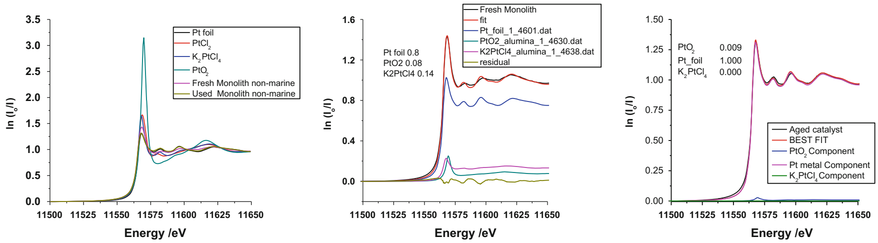


Fig. 6 Comparison of Pt L_3 XANES spectra of fresh and road aged (non-coastal) Diesel VEC catalysts (on the *left*) obtained from EU sources, with selected model compounds are shown here. In the middle, a linear combination fit obtained from the best fit for the fresh catalyst and on the right for the road aged catalyst are shown

K_2PtCl_4 data is shown in Fig. 6. In all the VEC catalyst samples, mixed information is obtained. For example, for the fresh catalysts the analysis suggests that the majority of the species is Pt^o and a minor component can either be due to Pt-Cl or Pt-O species or a combination of both. It is important to note that although the linear combination data calculated matches the white-line area, features at higher energies could not be matched precisely using this combination. Attempts were made to use other types of Pt-Cl compounds but the best fits were again not completely satisfactory. This may be due to the use of crystalline bulk materials data as the reference while the XANES features may have been affected by the high PGM dispersion in the VEC catalysts, as well as a Pt/Pd alloying effect. Based on chemical analysis, it was found that chlorine content (*ca.* 25 ppm) in the fresh sample is well below what would be stoichiometrically required by any Pt-Cl species indicated by the XANES data of the fresh and road aged catalyst.

We found the analysis of the EXAFS data is much more reliable in determining Pt speciation in the material, since the Pt-O, Pt-Cl and Pt-Pt distances are significantly different (2.02, 2.31 and 2.74 Å, respectively). We analysed the EXAFS data in detail to determine the species present in the catalysts; both fresh and road aged catalysts. The results of the best fit between computed and experimental data along with their respective FT's are shown in Fig. 7. The results of the analysis are given in Table 4.

It is clear from the structural parameters listed in Table 4 that the major components in all the catalysts are metallic species. One of the catalysts suggested the presence of a bimetallic Pt-Pd component, in addition to mono metallic Pt-Pt; which is easily distinguishable in the analysis of EXAFS data, despite the fact that Pt-Pt and Pd-Pd (including the bimetallic components) distances are closely similar. The other minor components seen can only be fitted to respective Pt-O distances. When an attempt was made to include a Pt-Cl component in the analysis it always yielded both unrealistic Pt-Cl distances (much shorter than expected) and also unrealistic Debye-Waller factors. Based on the detailed analysis of structural parameters, we infer that chloroplatinate species were not detected in either fresh or road aged VEC catalysts.

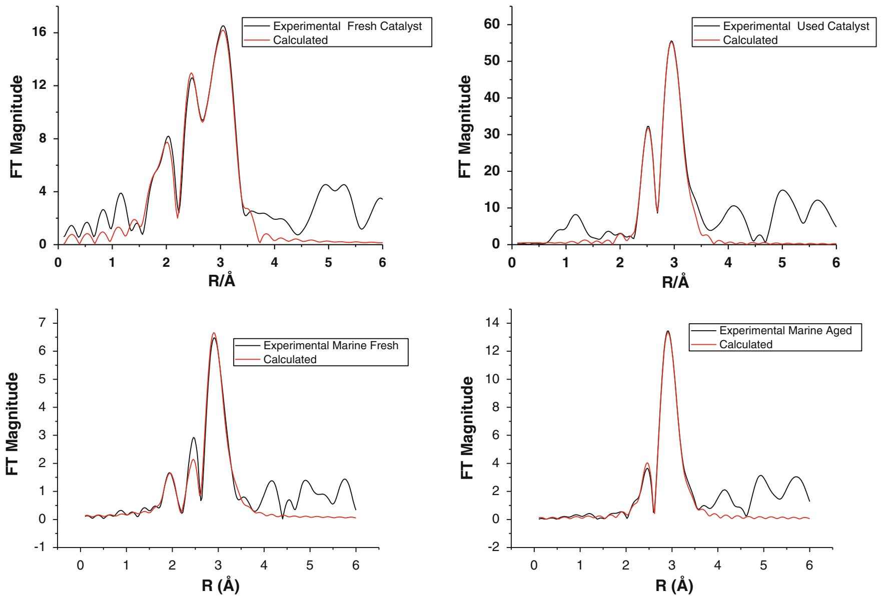


Fig. 7 Fourier transform of the best fit between experimental and computed EXAFS of non-coastal (*top*) and coastal (*bottom*) are shown here. Diesel VEC catalyst samples from EU sources; fresh (*top left*), road aged (*top right*), fresh (*bottom left*) and road aged (*bottom right*)

Table 4 Structural parameters obtained from analysis of Pt L_3 EXAFS data of EU-VEC diesel catalysts

VEC system	Atom-pair	Coordination number N	Interatomic distance R (Å)	Debye Waller FACTOR σ^2 (Å^2)	Fit index
Fresh non-coastal	Pt-O	1.71	2.01	0.009	42
	Pt-Pt	3.63	2.74	0.0055	
	Pt-Pd	1.53	2.74	0.0055	
Road aged non-coastal	Pt-Pt	7.44	2.71	0.0045	35
	Pt-Pd	2.71	2.74	0.0045	
Fresh coastal	Pt-O	0.7	2.0	0.005	47
	Pt-Pt	7.11	2.76	0.006	
Road aged coastal	Pt-O	0.38	1.98	0.004	37
	Pt-Pt	10.8	2.76	0.0045	

6 TWC Catalysts from North America

Chemical analysis of the TWC catalysts revealed the complex nature of the system. In particular, these solids were found to contain a large range of elements that contribute to a functioning automotive catalyst. While platinum content is found to be of the order of 700 ppm (along with some Rh component of *ca*. 125 ppm), large amounts of nickel were also found and both these elements can form bimetallic species with Pt. We ignore the presence of other components in our analysis with respect to the Pt edge, since they are unlikely to form an alloy with Pt species. The main components from the chemical analysis were found to be Pt, Rh and Ni in all the three catalysts—TWC Fresh, road-aged from a vehicle mainly driven in mid-west of USA (code: TWC ANC) and mainly driven in the coastal area (TWC AC). Other components include Ce, Zr which are both likely to be from the support oxide material. Analysis of the XAS data was performed at both the Pt L3 and L2 on both the fresh, and respective road-aged catalysts (more detailed analysis and other edges are given in Ref (Ash et al. 2014)). Here we show only the analysis using Pt L3 and L2 edge results and furthermore our aim is to show that the presence or absence of chloroplatinate species in the road-aged catalyst which is of environmental concern.

Typical Pt L3 and L2 XANES data are shown in Fig. 8 along with some model compounds representing the oxidic and metallic phases. Comparison of the L3 and L2 Edge XANES of TWC ANC and TWC AC with TWC fresh catalyst and Pt foil reveal that there are some differences in the white-line intensity. Data from the TWC Fresh sample match well with the XANES of the PtO_2 standard material suggesting that in the fresh catalyst platinum is present as an oxidic species, similar to the observation seen with all the other edges (Rh and Ni). However, upon road usage both Pt L2 and L3 edge XANES resemble that of metallic platinum with a trend in the white line peak intensity appears to follow TWC fresh ≫ TWC ANC > TWC AC > Pt foil. The increase in white line intensity has been described as being due to the increase in density of unoccupied states, which may be related to the presence of platinum in a higher oxidation state bonded to low Z scatterers

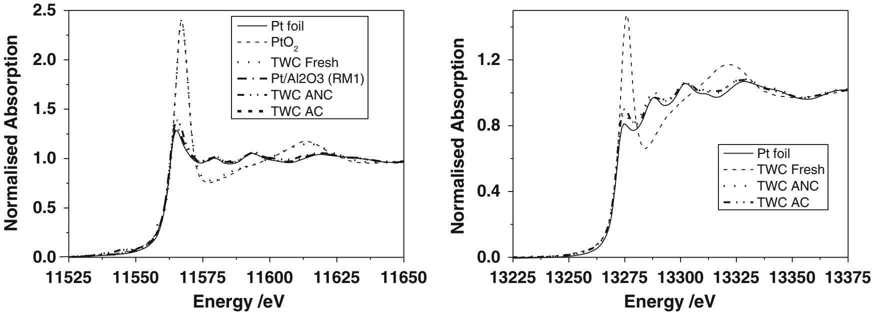


Fig. 8 Pt L3 (*left*) and L2 (*right*) edge XANES of North American sourced TWC catalysts along with several model compounds are given

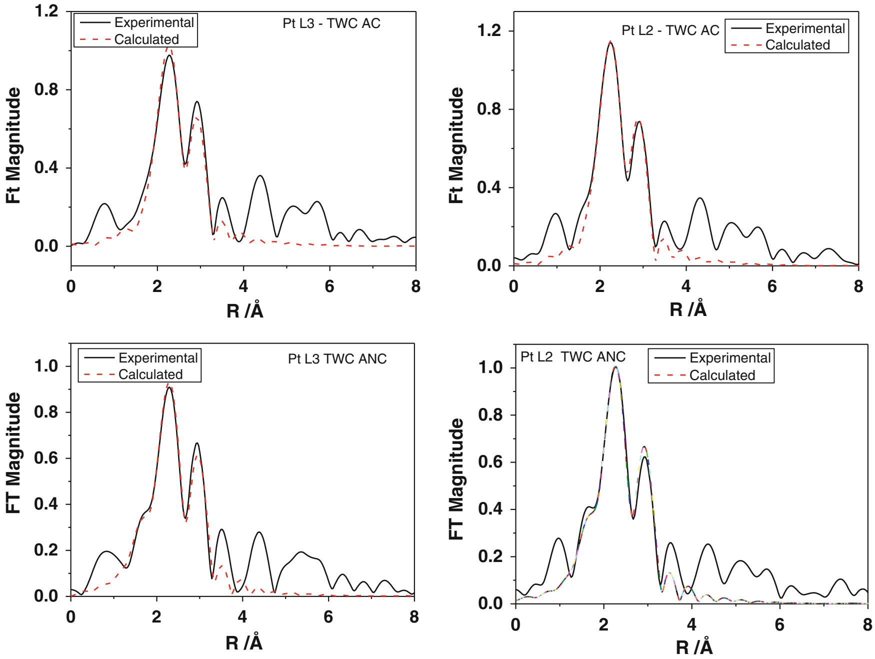


Fig. 9 Fourier transform of the best fit between experimental and computed Pt L3 and L2 EXAFS of road aged North American sourced TWC AC (*top*) and ANC catalysts (*bottom*)

(Russell and Rose 2004). However, it is difficult to precisely determine which type of compound with a specific low Z scatterer is responsible for the increase in the white line intensity. Furthermore, the presence of nanoparticles and nanoalloying may also contribute to differences in the Pt absorption edge (Russell and Rose 2004). Hence analysis through the LCF method may not produce reliable results (Hyde et al. 2011) and we therefore focused our analysis by examining the respective EXAFS data. Once again, combined Pt L3 and L2 edge data were analysed together to obtain a single structural model for all the catalysts. In Fig. 8 we show the best fit obtained for respective TWC road aged catalysts. We show only the road-aged catalysts here, since the XANES data of the TWC fresh catalyst clearly showed only the presence of platinum oxide species.

We systematically carried out the analysis of both TWC AC and TWC ANC data. In Fig. 9, we show the Fourier Transform of the best fit between experimental and calculated data for the aged TWC catalysts and the results of the analysis are given in Table 5. First we analysed Pt L-edge EXAFS data by considering only Pt as its only neighbour, since it is the dominant component. However, the match between the experiment and calculated model was found to be unsatisfactory, (R-factor is *ca.* 0.015), which indicated there may be more than one type of neighbour present around the platinum present in the catalysts. We systematically introduced all the possible near neighbours, in particular O, Cl (although chemical analysis ruled out the presence of Cl, it is our aim to determine whether any Cl associated with Pt is present in the system), Rh and Ni (these metals are two of the other major metallic components in the catalysts). Inclusion of any of these elements on its own slightly improves the quality of the fit (R-factor was used as one of the criteria) but in some cases, for example, inclusion of oxygen and chlorine did not produce physically meaningful bond distances or Debye-Waller factors (in many instances a large positive or negative value is obtained which we do not consider to be meaningful). Inclusion of Rh improved the quality of the fit as well as producing acceptable values for a typical Pt-Rh distance. Similarly inclusion of Ni along with Rh improved the quality of the fit with acceptable distances. The concentrations of such bimetallic species were found to be between 5 and 10 %. We did not find any clear evidence for Rh-Pt and Ni-Pt from the Rh and Ni K-edges, respectively, since the amounts of reduced Rh and Ni were found to be of the order of 10 %, with the dominant species being oxides of nickel and rhodium. Similar observation was made for a Pt-Rh catalyst where the Rh edge did not show any Rh-Pt component, whereas the Pt-edge results indicated the presence of a Pt-Rh interaction. This may be due to the formation of specific core-shell type structures rather than an alloy. Therefore, we conclude that, due to the complex nature of the catalytic material and presence of a variety of elements, it is difficult to precisely determine which type of neighbour is present around platinum in addition to metallic platinum. We also wish to note that there are sulfur and phosphorus

Table 5 Structural parameters obtained from the analysis of combined refinement of Pt L3 and Pt L2-edge EXAFS data of road aged North American sourced three way catalysts, TWC AC and TWC ANC

Catalyst Name	Edge	Atom-Pair	N	R (Å)	σ^2 (Å^2)	*R*-factor
TWC ANC	Pt L3	Pt-Pt	6.3	2.75	0.0056	0.0053
		Pt-Rh	1.2	2.72	0.0056	
		Pt-Ni	0.5	2.66	0.0056	
		Pt-O	0.5	1.96	0.004	
	Pt L2	Pt-Pt	6.9	2.75	0.0056	
		Pt-Rh	1.4	2.72	0.0056	
		Pt-Ni	0.5	2.66	0.0056	
		Pt-O	0.6	1.96	0.004	
TWC ANC	Pt L3	Pt-Pt	6.2	2.74	0.0047	0.006
		Pt-Rh	1.2	2.69	0.0047	
		Pt-Ni	0.6	2.61	0.0047	
	Pt L2	Pt-Pt	6.9	2.74	0.0047	
		Pt-Rh	1.3	2.69	0.0047	
		Pt-Ni	0.7	2.61	0.0047	

components in addition to carbon also present in the road-aged catalysts, which may also interact with platinum.

From Table 5 it is clear that apart from the metallic platinum species, some alloy components are also present. The bond distances between Pt and Rh or Ni appear to be similar to the one expected for a bimetallic component. Although their concentrations are relatively low, without including them in the model it was not possible to obtain a good fit between experimental and computed EXAFS. It is interesting to see the presence of small amounts of Pt-O species in the TWC ANC catalysts and inclusion of similar oxidic component in the TWC AC catalysts data did not improve the goodness of fit. This is also consistent with the observed XANES white line intensities where the TWC ANC data is slightly higher compared to TWC AC. As noted earlier, inclusion of Pt-Cl component (with others in various combinations of Pt-O, Pt-Rh, Pt-Ni and Pt-Pt) in the analysis of the EXAFS data did not yield a good fit between experimental and computed EXAFS with a typical Pt-Cl bond distance of *ca.* 2.3 Å and a Debye-Waller factor of between 0.001 and 0.015 Å^2(in some instances negative values for the Debye-Waller factor were obtained or were too large to be considered). Based on this analysis that the Pt-Cl component is not present in a detectable amount, which we estimate to be less than 5 % with respect to total platinum components in the sample.

To substantiate the absence of chlorine associated with platinum we carried out a XANES study at the Cl K-edge, which we consider as an important aspect to be considered to establish the presence or absence of chloroplatinate species. Typical XANES spectra of selected chloroplatinate compounds are given in Fig. 10 (left). There are two distinct features (Aliaga-Alcalde et al. 2009; Rumpf et al. 1999) seen in all the reference compounds used in this study: a pre-edge peak region marked 'P' and a main edge marked 'M'.

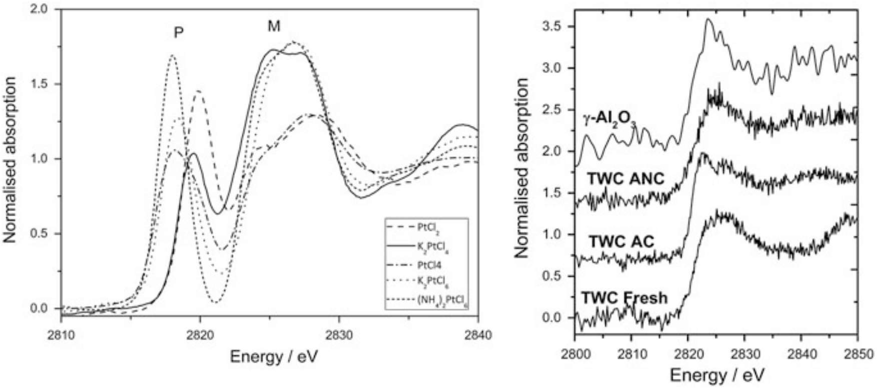


Fig. 10 Cl K-edge XANES of selected reference compounds containing platinum (*left*) and Fresh and Road Aged North American sourced TWC along with γ-alumina reference (*right*) are shown here

In Fig. 10 (right) we also plot the Cl K-edge XANES of the three TWC catalysts, Fresh, AC and ANC along with the γ–alumina reference material. Firstly the fluorescence counts for respective TWC catalysts were found to be fairly low suggesting the presence of very low concentrations of chlorine in the catalysts. Extraction of the data after summing several spectra showed only a main edge and no evidence for a pre-edge peak feature seen in all the platinum containing reference compounds. Similar XANES data was also seen for γ-alumina reference material which did not contain platinum or any other metal suggesting that the chlorine present in the system is not associated with platinum.

7 Conclusions

XANES and EXAFS analysis using the Pt L3 and L2 edges of Fresh TWC and diesel VEC catalysts, reveal that platinum and any other metal present in the fresh catalysts are present as oxidic species. Road aged (used) catalysts showed mainly reduced platinum as the major species. However, depending on the amounts of palladium in the catalysts, alloys of Pt-Pd were found in the diesel oxidation catalysts; some fraction of palladium in these catalysts was found to be still oxidic in nature. On the other hand road aged TWC catalysts were found to be complex in nature with metallic form as the major species in the catalysts; additional species, in particular related alloys with Rh and Ni, may also be present in the catalysts. Based on the analysis of the Pt edge EXAFS and more importantly Cl K-edge XANES, we conclude that chloroplatinate species is not present in any significant amount that may affect the environment.

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References

Aksenov VL, Koval’chuk MV, Kuz’min AY, Purans Y, Tyutyunnikov SI (2006) Development of methods of EXAFS spectroscopy on synchrotron radiation beams: review. Crystallogr Rep 51 (6):908–935. doi:10.1134/s1063774506060022

Aliaga-Alcalde N, George SD, Alfaro-Fuentes I, Cooper GJT, Barba-Behrens N, Bernes S, Reedijk J (2009) Physical characterization and biological studies of a (streptidine) ((PtCl4)-Cl-II) compound. Polyhedron 28(16):3459–3466. doi:10.1016/j.poly.2009.07.022

Ankudinov AL, Ravel B, Rehr JJ, Conradson SD (1998) Real-space multiple-scattering calculation and interpretation of X-ray-absorption near-edge structure. Phys Rev B 58(12):7565–7576

Ankudinov AL, Rehr JJ, Bare SR (2000) Hybridization peaks in Pt-Cl XANES. Chem Phys Lett 316(5–6):495–500

Ankudinov AL, Rehr JJ, Low JJ, Bare SR (2001) Pt L-edge XANES as a probe of Pt clusters. J Synchrotron Radiat 8:578–580

Ash PW, Boyd DA, Hyde TI, Keating JL, Randlshofer G, Rothenbacher K, Sankar G, Schauer JJ, Shafer MM, Toner BM (2014) Local structure and speciation of platinum in fresh and road-aged North American sourced vehicle emissions catalysts: an X-ray absorption spectroscopic study. Environ Sci Technol 48(7):3658–3665. doi:10.1021/es404974e

Bare SR, Ressler T (2009) Characterization of catalysts in reactive atmospheres by X-ray absorption spectroscopy. In: Gates BC, Knozinger H (eds) Advances in catalysis, vol 52. Elsevier Academic Press Inc.: San Diego, pp 339–465. doi:10.1016/s0360-0564(08)00006-0

Burch R, Breen JP, Meunier FC (2002) A review of the selective reduction of NOx, with hydrocarbons under lean-burn conditions with non-zeolitic oxide and platinum group metal catalysts. Appl Catal B Environ 39(4):283–303

Catalytic Converters (2014) international platinum group metals association. http://www.ipa-news.com/en/89-0-Catalytic-Converters.htm. Accessed 6th June 2014

Chen X, Chu W, Wang L, Wu Z (2009) Geometry of Pt(IV) in H(2)PtCl(6) aqueous solution: An X-ray absorption spectroscopic investigation. J Mol Struct 920(1–3):40–44

Dent AJ, Diaz-Moreno S, Evans J, Fiddy SG, Jyoti B, Newton MA (2005) In situ monitoring of oxide-supported platinum-group metal catalysts by energy dispersive EXAFS. Phys Scr T115:72–75

Ezekoye OK, Drews AR, Jen HW, Kudla RJ, McCabe RW, Sharma M, Howe JY, Allard LF, Graham GW, Pan XQ (2011) Characterization of alumina-supported Pt and Pt-Pd NO oxidation catalysts with advanced electron microscopy. J Catal 280(1):125–136

Feldmann J, Salaun P, Lombi E (2009) Critical review perspective: elemental speciation analysis methods in environmental chemistry—moving towards methodological integration. Environ Chem 6(4):275–289. doi:10.1071/en09018

Fernandez-Garcia M (2002) Xanes analysis of catalytic systems under reaction conditions. Catal Rev Sci Eng 44(1):59–121. doi:10.1081/cr-120001459

Gomez B, Palacios MA, Gomez M, Sanchez JL, Morrison G, Rauch S, McLeod C, Ma R, Caroli S, Alimonti A, Petrucci F, Bocca B, Schramel P, Zischka M, Petterson C, Wass U (2002) Levels and risk assessment for humans and ecosystems of platinum-group elements in the airborne particles and road dust of some European cities. Sci Total Environ 299(1–3):1–19. doi:10.1016/s0048-9697(02)00038-4

Graefe M, Donner E, Collins RN, Lombi E (2014) Speciation of metal(loid)s in environmental samples by X-ray absorption spectroscopy: A critical review. Anal Chim Acta 822:1–22. doi:10.1016/j.aca.2014.02.044

Henderson GS, de Groot FMF, Moulton BJA (2014) X-ray Absorption Near-Edge Structure (XANES) Spectroscopy. In: Henderson GS, Neuville DR, Downs RT (eds) Spectroscopic methods in mineralogy and materials sciences. Reviews in mineralogy and geochemistry, vol 78. Mineralogical Society of America, Chantilly, VA, pp 75–138. doi:10.2138/rmg.2014.78.3

Hyde TI, Ash PW, Boyd DA, Randlshofer G, Rothenbacher K, Sankar G (2011) X-ray absorption spectroscopic studies of platinum speciation in fresh and road aged light-duty diesel vehicle emission control catalysts. Platin Met Rev 55(4):233–245. doi:10.1595/147106711x598910

Kaneeda M, Iizuka H, Hiratsuka T, Shinotsuka N, Arai M (2009) Improvement of thermal stability of NO oxidation Pt/Al(2)O(3) catalyst by addition of Pd. Appl Catal B-Environ 90 (3–4):564–569

Kaspar J, Fornasiero P (2003) Nanostructured materials for advanced automotive de-pollution catalysts. J Solid State Chem 171(1–2):19–29. doi:10.1016/s0022-4596(02)00141-x

Kaspar J, Fornasiero P, Hickey N (2003) Automotive catalytic converters: current status and some perspectives. Catal Today 77(4):419–449. doi:10.1016/s0920-5861(02)00384-x

Koningsberger DC, Prins R (1988) X-Ray absorption: principles, applications, techniques of EXAFS, SEXAFS and XANES. Chemical analysis: a series of monographs on analytical chemistry and its applications. Wiley, New York

Leggett D (2013) UK: global vehicle sales up 5.2 % to 80.9 m in 2012. Aroq Ltd. http://www.just-auto.com/news/global-vehicle-sales-up-52-to-809m-in-2012_id130772.aspx. Accessed 6 June 2014

Lei Y, Jelic J, Nitsche LC, Meyer R, Miller J (2011) Effect of Particle Size and Adsorbates on the L(3), L(2) and L(1) X-ray absorption near edge structure of supported Pt nanoparticles. Top Catal 54(5–7):334–348

Levy PJ, Pitchon V, Perrichon V, Primet M, Chevrier M, Gauthier C (1998) Characterisation of model three-way catalysts—II. Infrared study of the surface composition of platinum-rhodium alumina catalysts. J Catal 178(1):363–371

Li Z, Dervishi E, Saini V, Zheng L, Yan W, Wei S, Xu Y, Biris AS (2010) X-ray absorption fine structure techniques. Part Sci Technol 28(2):95–131. doi:10.1080/02726350903328944

Manceau A, Marcus MA, Grangeon S (2012) Determination of Mn valence states in mixed-valent manganates by XANES spectroscopy. Am Mineral 97(5–6):816–827. doi:10.2138/am.2012.3903

Moldovan M, Gomez MM, Palacios MA (1999) Determination of platinum, rhodium and palladium in car exhaust fumes. J Anal At Spectrom 14(8):1163–1169. doi:10.1039/a901516g

Moldovan M, Palacios MA, Gomez MM, Morrison G, Rauch S, McLeod C, Ma R, Caroli S, Alimonti A, Petrucci F, Bocca B, Schramel P, Zischka M, Pettersson C, Wass U, Luna M, Saenz JC, Santamaria J (2002) Environmental risk of particulate and soluble platinum group elements released from gasoline and diesel engine catalytic converters. Sci Total Environ 296 (1–3):199–208. doi:10.1016/s0048-9697(02)00087-6

Moldovan M, Rauch S, Morrison GM, Gomez M, Palacios MA (2003) Impact of ageing on the distribution of platinum group elements and catalyst poisoning elements in automobile catalysts. Surf Interface Anal 35(4):354–359. doi:10.1002/sia.1541

Nagai Y, Dohmae K, Ikeda Y, Takagi N, Tanabe T, Hara N, Guilera G, Pascarelli S, Newton MA, Kuno O, Jiang H, Shinjoh H, Matsumoto Si (2008) In Situ redispersion of platinum autoexhaust catalysts: an on-line approach to increasing catalyst lifetimes? Angew Chem-Int Ed 47 (48):9303-9306

Newton MA, van Beek W (2010) Combining synchrotron-based X-ray techniques with vibrational spectroscopies for the in situ study of heterogeneous catalysts: a view from a bridge. Chem Soc Rev 39(12):4845–4863

Palacios M, Gomez MM, Moldovan M, Morrison G, Rauch S, McLeod C, Ma R, Laserna J, Lucena P, Caroli S, Alimonti A, Petrucci F, Bocca B, Schramel P, Lustig S, Zischka M, Wass U, Stenbom B, Luna M, Saenz JC, Santamaria J (2000) Platinum-group elements: quantification in collected exhaust fumes and studies of catalyst surfaces. Sci Total Environ 257(1):1–15. doi:10.1016/s0048-9697(00)00464-2

Platinum Johnson Matthey PLC (2013). http://www.platinum.matthey.com/media/1614079/platinum_2013.pdf. Accessed 6 June 2014

Prichard HM, Fisher PC (2012) Identification of platinum and palladium particles emitted from vehicles and dispersed into the surface environment. Environ Sci Technol 46(6):3149–3154. doi:10.1021/es203666h

Rauch S, Hemond HF, Barbante C, Owari M, Morrison GM, Peucker-Ehrenbrink B, Wass U (2005) Importance of automobile exhaust catalyst emissions for the depostion of platinum, palladium, and rhodium in the Northern Hemisphere. Environ Sci Technol 39(21):8156–8162

Rogemond E, Essayem N, Frety R, Perrichon V, Primet M, Chevrier M, Gauthier C, Mathis F (1999) Characterization of model three-way catalysts—III. Infrared study of the surface composition of platinum-rhodium ceria-alumina catalysts. J Catal 186(2):414–422

Roy S, Baiker A (2009) NOx storage-reduction catalysis: from mechanism and materials properties to storage-reduction performance. Chem Rev 109(9):4054–4091. doi:10.1021/cr800496f

Rumpf H, Hormes J, Moller A, Meyer G (1999) Thermal decomposition of $(NH_4)(2)$ PtCl6—an in situ X-ray absorption spectroscopy study. J Synchrotron Radiat 6:468–470. doi:10.1107/s0909049598015994

Russell AE, Rose A (2004) X-ray absorption spectroscopy of low temperature fuel cell catalysts. Chem Rev 104(10):4613–4635. doi:10.1021/cr020708r

Sa J, Abreu Fernandes DL, Aiouache F, Goguet A, Hardacre C, Lundie D, Naeem W, Partridge WP, Stere C (2010) SpaciMS: spatial and temporal operando resolution of reactions within catalytic monoliths. Analyst 135(9):2260–2272

Sen IS (2013) Platinum group element pollution is a growing concern in countries with developing economy. Environ Sci Technol 47(24):13903–13904

Thomas JM, Sankar G (2001a) The role of synchrotron-based studies in the elucidation and design of active sites in titanium-silica epoxidation catalysts. Acc Chem Res 34(7):571–581. doi:10.1021/ar010003w

Thomas JM, Sankar G (2001b) The role of XAFS in the in situ and ex situ elucidation of active sites in designed solid catalysts. J Synchrotron Radiat 8:55–60

Twigg MV (2006) Roles of catalytic oxidation in control of vehicle exhaust emissions. Catal Today 117(4):407–418

Twigg MV (2011a) Catalytic control of emissions from cars. Catal Today 163(1):33–41

Twigg MV (2011b) Haren Gandhi 1941–2010: contributions to the development and implementation of catalytic emissions control systems. Platin Met Rev 55(1):43–53. doi:10.1595/147106711x540652

Twigg MV, Phillips PR (2009) Cleaning the air we breathe—controlling diesel particulate emissions from passenger cars. Platin Met Rev 53(1):27–34. doi:10.1595/147106709x390977

Working in Partnership for Cleaner Air (2014) Association for emissions control by catalysts. http://www.aecc.eu/en/default.html. Accessed 6 June 2014

Part IV
Environmental Bioavailability and Biomonitoring of PGE

Bioavailability of Platinum Group Elements to Plants—A Review

Nadine Feichtmeier and Kerstin Leopold

Abstract In this review article we have summarised the results of platinum group element (PGE) uptake studies and measurement of PGE contents in plants published within the last 5 years. Most studies consider thereby exposure of plants to platinum (Pt), palladium (Pd) and rhodium (Rh) resulting from traffic-related emission. However, some studies deal with Pt contamination arising from its application in cytostatics. In the following we will first discuss analytical tools for determination of PGE traces in plant material and then give an overview of PGE concentrations in plants from contaminated field sites. Moreover, different methodologies applied in exposure studies (PGE species, nutrients, growing parameters) as well as the resulting effects on exposed plants are presented.

1 Analytical Methods

The determination of platinum (Pt), palladium (Pd) and rhodium (Rh) in soil and dust samples has been subject of analytical efforts for the last decades, while less attention was paid to other matrices of environmental significance, such as plants and animals. However, the examination of plant tissues is of growing interest due to the observed bioaccumulation of PGEs in plants.

The following section will give an overview on analytical methods that were applied for the analysis of Pt, Pd and Rh in plant materials. Thereby, three main issues are addressed: 1. Determination of PGE concentration; 2. Investigation of uptake of different chemical PGE species (nanoparticles, agglomerates, ions etc.); 3. Localization of PGEs within the plant.

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Environmental Science and Engineering, DOI 10.1007/978-3-662-44559-4_20

1.1 Determination of PGE Concentration

The determination of PGEs at environmentally and biologically relevant concentrations is still a challenge for analytical chemists. Sensitive and interference-free analytical methods with high sensitivity are required for measuring the very low levels of Pt, Pd, and Rh in contaminated materials (ng kg^{-1} range) and for the estimation of background concentrations (Moldovan 2007; Bencs et al. 2003). In Table 1 analytical methods for sample preparation and detection are listed that were applied for the determination of palladium, platinum and/or rhodium in different plant species. Instrumental detection techniques, such as inductively coupled plasma—mass spectrometry (Hooda et al. 2008; Odjegba et al. 2007; Rose et al. 2010; Tankari Dan-Badjo et al. 2007; Rauch and Fatoki 2013; Pan et al. 2009; Hooda et al. 2007; Cyprien et al. 2008; Tankari Dan-Badjo et al. 2008; Bonanno 2011; Pino et al. 2010) or—optical emission spectrometry (Niemelä et al. 2007; Nischkauer et al. 2013) (ICP-MS /ICP-OES), electrothermal vaporization inductively coupled plasma—optical emission spectrometry (Nischkauer et al. 2013) (ETV ICP-OES), electro thermal atomic absorption spectrometry (Sánchez Rojas et al. 2009; Diehl and Gagnon 2007; Akrivi et al. 2012; Papa et al. 2010; Bosch Ojeda et al. 2007; Speranza et al. 2010; Battke et al. 2008; Leopold and Schuster 2010; Fumagalli et al. 2010) (ETAAS), or adsorptive stripping (Orecchio and Amorello 2010) and differential pulse voltammetry (Orecchio and Amorello 2010; Kolodziej et al. 2007; Supalkova et al. 2008; Mikulaskova et al. 2013) are powerful tools in this regard. Thereby, ICP-MS, ETAAS and ICP-OES serve for the detection of palladium, platinum and rhodium, while application of differential pulse and adsorptive stripping voltammetry is restricted to the detection of Pt or Rh because of the irreversibility of electrode processes for Pd (Georgieva and Pilar 1997).

For most detection techniques, appropriate sample preparation steps are required to ensure quantitative transformation of the analytes into soluble species and/or separation from interfering compounds. Typically, ICP-OES and ICP-MS require total digestion of the plant material in order to obtain liquid samples. For application of electroanalytical techniques, however, in addition complete mineralisation of organic matter is essential for interference-free measurement. For this purpose, mainly wet digestion by application of oxidazing acids is used, often pressure- and/or microwave-assisted (Odjegba et al. 2007; Rauch and Fatoki 2013; Pan et al. 2009; Tankari Dan-Badjo et al. 2008; Diehl and Gagnon 2007; Fumagalli et al. 2010; Kolodziej et al. 2007; Haus et al. 2009). Alternatively, extraction from solid samples can be performed prior to measurement (Supalkova et al. 2008). In any case, due to low concentrations of PGEs expected in biological materials and the dilutive effect of wet digestion, pre-concentration of the analyte is typically required. Here, flow injection analysis systems for selective pre-concentration should be named as most commonly applied techniques (Sánchez Rojas et al. 2009; Bosch Ojeda et al. 2007; Battke et al. 2008). An alternative approach was presented by Nischkauer et al. (2013) who developed a method for detection of PGE in rapeseed by carbonisation of the solid plant samples in a muffle oven prior to

Table 1 Summary of analytical methods for detection of platinum group elements in plant material

Detection technique	Plant species	Pre-treatment	Limit of detection (LOD) in ng g^{-1} unless stated otherwise	Validation	References
ETAAS	Bignonia	Spiked with Pd(II) and/or Rh(III) standard solutions; Microwave-assisted digestion with HNO_3/H_2O_2; Evaporation; Dissolution in DI water; Flow injection pre-concentration	NA	Recovery experiments with spiked samples: Pd: 103.5 % Rh: 100.3 %	Sánchez Rojas et al. (2009)
		Spiked with Pt; Microwave-assisted digestion with HNO_3; Evaporation; Dissolution with DI water; Flow injection pre-concentration	Pt: 2 ng mL^{-1}	Recovery experiments with spiked samples: 106 %	Bosch Ojeda et al. (2007)
	Pinus	Spiked with Pd(II) and/or Rh(III) standard solutions; Microwave-assisted digestion with HNO_3/H_2O_2; Evaporation; Dissolution in DI water; Flow injection pre-concentration	NA	Recovery experiments with spiked samples: Pd: 101.8 % Rh: 104.7 %	Sánchez Rojas et al. (2009)
		Spiked with platinum; Microwave-assisted digestion with HNO_3; Evaporation; Dissolution with DI water; Flow injection pre-concentration	Pt: 2 ng mL^{-1}	Recovery experiments with spiked samples: 98.4 %	Bosch Ojeda et al. (2007)
	Barley (*Hordeum vulgare L.*)	Pressurized microwave-assisted digestion with HNO_3/H_2O_2; Flow injection pre-concentration	Pd: 3.275	Recovery experiments with spiked samples: 100 ± 9 %	Battke et al. (2008)
			Pd: 13.2 μg L^{-1}; 16 ng L^{-1} (in case of pre-concentration)	NA	Leopold and Schuster (2010)
	Grass (family *Gramineae*)	Microwave-assisted digestion with HNO_3, HF; Treated with H_3BO_3; Filtration; Washing with HNO_3	Pd: <1 Pt: <2 Rh: <1	NA	Akrivi et al. (2012)

(continued)

Table 1 (continued)

Detection technique	Plant species	Pre-treatment	Limit of detection (LOD) in ng g^{-1} unless stated otherwise	Validation	References
	Lettuce	Spiked with Pd(II) and/or Rh(III) standard solutions; Microwave-assisted digestion with HNO_3/H_2O_2; Evaporation; Dissolution in DI water; Flow-injection pre-concentration	NA	Recovery experiments with spiked samples: Pd: 104.4 % Rh: 102.0 %	Sánchez Rojas et al. (2009)
	Canadian water-weed (*Elodea canadensis*)	Digestion with HNO_3; Heating until near-dryness; Dissolution with HNO_3	NA	NA	Diehl and Gagnon (2007)
	Green arrow arum (*Peltandra virginica*)				
	Wild carot (*Daucus carota*)	Hot digestion with HNO_3			
	Holm-oak (*Quercus ilex L.*)	Microwave-assisted digestion with aqua regia	NA	Recovery in standard reference materials: 90–100 %	Papa et al. (2010)
	Lentil	Spiked with Pt; Microwave-assisted digestion with HNO_3; Evaporation; Dissolution with DI water; Flow injection pre-concentration	Pt (LOQ): 2–4 µg L^{-1}	Recovery experiments with spiked samples: 100 %	Bosch Ojeda et al. (2007)
	Rice				
	Kiwifruit pollen (*Actinidia deliciosa var. deliciosa*)	Centrifugation ($PdCl_2$-treated samples) or vacuum filtration (Pd-NP-treated samples); Washing with basal medium; Microwave-assisted digestion with HNO_3/H_2O_2	Pd: 13.2 µg L^{-1}	NA	Speranza et al. (2010)
	Cherry laurel (*Prunus laurus cerasus*)	Incineration in porcelain crucible; Digestion with HCl/H_2O_2; Evaporation to near-dryness; Treated with aqua regia; Reducing to near dryness; Addition of HCl and DI water	Pd: 1.83 µg L^{-1} Pt: 1.20 µg L^{-1} Rh: 0.99 µg L^{-1}	Recovery in milled auto catalyst reference material SRM 2556: Values not given; Found values within the limits of standard deviation	Fumagalli et al. (2010)

(continued)

Table 1 (continued)

Detection technique	Plant species	Pre-treatment	Limit of detection (LOD) in ng g^{-1} unless stated otherwise	Validation	References
ICP-MS	Grass (*Aristida bipartita, Bothriochloa insculpta, Digitaria eriantha, Ischaemum afrum, Panicum maximum*)	Microwave-assisted digestion with aqua regia; Heating to dryness; Dissolution in HCl	NA	Recovery in road dust reference material BCR-723 92.6 %	Rauch and Fatoki (2013)
		Nickel sulfide fire assay for pre-conentration; Crucible treated with H_2O; Dissolution and heating in HCl; Filtration; Dissolution in HNO_3	NA	Recovery in reference material GBW 07294: Pt: 91.1 %; Pd: 101 %; Rh: 98.2 %	Pan et al. (2009)
	Cocksfoot grass (*Dactylis glomeratus*)	Microwave-assisted digestion with HNO_3/H_2O_2	Pd: 0.185 Pt: 0.105 Rh: 0.07	Recovery: 100 ± 8 %	Hooda et al. (2008)
		Microwave-assisted digestion with HNO_3/H_2O_2; Filtration	Pd: 0.185 Pt: 0.105 Rh: 0.07	Recovery with soil digestate collected outside Oxford: Pd: 108 % Pt: 97 % Rh: 104 %	Hooda et al. (2007)
	Ryegrass (*Lolium perenne*)	Microwave-assisted digestion with $HNO_3/H_2O_2/H_2O$	Pd (LOQ): 0.5 Pt (LOQ): 0.25 Rh (LOQ): 0.25	NA	Tankari Dan-Badjo et al. (2007)
		Microwave-assisted digestion with $HNO_3/H_2O_2/H_2O$	Pd (LOQ): 0.5 Pt (LOQ): 0.25 Rh (LOQ): 0.25	NA	Tankari Dan-Badjo et al. (2008)
	Lettuce	Treated with HNO_3/HCl; Heating to near-dryness; Treated with HNO_3; Heating under reflux; Filtration	NA	NA	Odjegba et al. (2007)

(continued)

Table 1 (continued)

Detection technique	Plant species	Pre-treatment	Limit of detection (LOD) in ng g^{-1} unless stated otherwise	Validation	References
	Mosses	Digestion with HNO_3/HCl; Heating under reflux; Filtration	Pd: 1 000 μg L^{-1} Pt: 2 000 μg L^{-1} Rh: 400 μg L^{-1}	Recovery experiments with spiked samples: Pd: 87–104 % Pt: 91–105 % Rh: 93–110 %	Cyprien et al. (2008)
	Maize	Digestion with HNO_3/HCl; Heating under reflux; Filtration; Spike with PGE standard solutions		Recovery experiments with spiked samples: Pd: 87–90 % Pt: 92–105 % Rh: 93 %	
	Dandelion	Digestion with HNO_3/HCl; Heating under reflux; Filtration		Recovery experiments with spiked samples: Pd: 87–104 % Pt: 91–105 % Rh: 93–110 %	
	Fern	Digestion with HNO_3/HCl; Heating under reflux; Filtration			
	Common reed (*Phragmites australis*)	Microwave-assisted digestion with HNO_3/H_2O_2	NA	Recovery in Lagorosiphon maior plant reference material BCR-060: Values not given; Found values within 10 % of the certified values	Bonanno (2011)
ICP-HR-MS	Green vegetables	Microwave-assisted digestion with HNO_3/HCl	Pd: 0.03–0.2 Pt: 0.5–3.0 Rh: 0.5–3.0	NA	Rose et al. (2010)
	Potatoes				
	Vegetables				
	Fresh fruits				
	Nuts				

(continued)

Table 1 (continued)

Detection technique	Plant species	Pre-treatment	Limit of detection (LOD) in ng g^{-1} unless stated otherwise	Validation	References
ICP-OES	Moss (*Pleurozium schreberi*)	Microwave-assisted digestion with HNO_3/H_2O_2, HCl/HF	Pt: 0.5 Rh: 0.2	Recovery in road dust reference material BCR-723: Pt: 98 ± 10 % Rh: 100 ± 13 %	Niemelä et al. (2007)
	Lucerne (*Medicago sativa*)	Ashing in air; Microwave-assisted digestion with HCl/HNO_3	NA	NA	Bali et al. (2010)
	Brown mustard (*Brassica juncea*)				
	Rapeseed (*Brassica napus*)	Microwave-assisted digestion with $HNO_3/HCl/H_2O_2/HF$	Pd: 0.72 µg g^{-1} Pt: 2.1 µg g^{-1} Rh: 1.33 µg g^{-1}	NA	Nischkauer et al. (2013)
Differential pulse voltammetry	Grass	Ashing on hot plate; Mineralisation with HNO_3; Treated with H_2SO_4; Filtration	NA	NA	Kolodziej et al. (2007)
	Lesser duckweed (*Lemna minor*)	Freezing in liquid nitrogen; Treated with phosphate buffer; Homogenization on vortex; Centrifugation; Filtration	Pt: 95 pmol L^{-1}	NA	Supalkova et al. (2008)
	Oleander (*Nerium oleander L.*)	Ashing in muffle; Pressurised microwave-assisted digestion with HNO_3/HCl	Pt: 0.30	NA	Orecchio and Amorello (2010)
Adsorptive stripping differential pulse voltammetry	Maize (*Zea mays L.*)	Microwave-assisted digestion with HNO_3/H_2O_2; Treated with acetate buffer	NA	NA	Mikulaskova et al. (2013)
	Pea (*Pisum sativum L.*)				

(continued)

Table 1 (continued)

Detection technique	Plant species	Pre-treatment	Limit of detection (LOD) in ng g^{-1} unless stated otherwise	Validation	References
Adsorptive stripping voltammetry	Oleander (*Nerium oleander L.*)	Ashing in muffle; Pressurized microwave-assisted digestion with HNO_3/HCl	Rh: 0.40	NA	Orecchio and Amorello (2010)
SF ICP-MS	Lichen (*Usnea barbata*)	Pre-digestion with $HNO_3/HClO_4$; Microwave-assisted digestion with $HNO_3/HClO_4$, HF/H_3BO_3	Pt: 0.013 Rh: 0.030	Recovery experiments with spiked samples: Pt: 98.5–102.4 % Rh: 100.2–106.0 %	Pino et al. (2010)
ETV ICP-OES	Rapeseed (*Brassica napus*)	Equilibration in airconditioned room; Carbonisation in muffle furnace	Pd: 0.14 μg g^{-1} Pt: 0.38 μg g^{-1} Rh: 0.13 μg g^{-1}	NA	Nischkauer et al. (2013)

(Including only work that has been published in 2007 and thereafter; Abbreviations: *ETAAS* Electrothermal atomic absorption spectrometry, *ICP-MS* Inductively coupled plasma mass spectrometry; *ICP-HR-MS* Inductively coupled plasma high-resolution mass spectrometry, *ICP-OES* Inductively coupled plasma optical emission spectrometry, *SF ICP-MS* Sector field inductively coupled plasma mass spectrometry, *ETV ICP-OES* Electrothermal vaporization inductively coupled plasma optical emission spectrometry, *DI* Deionized, *NA* Not available.)

measurement by ICP-OES. Detected PGE values were comparable to those received after microwave-assisted wet digestion and subsequent determination by ICP-OES.

Overall, quality assessment of the results is of great importance in order to assure reliability of the obtained results. The complexity of the matrix, the fact that PGEs are present only in trace amounts and the need for elimination of numerous interferents complicate precise and accurate analyses. Therefore, the investigation of certified reference materials (CRMs), interlaboratory studies, comparison of the results obtained by different analytical procedures, and recovery studies are to be used for evaluation of the quality of the results. Unfortunately, so far no suitable (plant) reference material is available for validation of analytical procedures for detection of PGE in plant material. Numerous CRMs exist for geological matrices containing PGEs at $\mu g\ g^{-1}$ concentrations. However, they do not cover the concentration ranges of PGEs in environmental materials nor provide comparable matrix compositions (Bencs et al. 2003). Road dust (BCR-723) is currently the only available certified reference material for PGEs at trace levels. Despite this fact, several studies prove the reliability of their results by recovery experiments, as there are e.g. interlaboratory measurements (Pan et al. 2009), investigation of milled automobile catalysts (SRM 2556) (Fumagalli et al. 2010), investigation of road dust (BCR-723) (Rauch and Fatoki 2013; Niemelä et al. 2007) or investigation of spiked well-defined plant material (aquatic plants, BCR-060) (Bonanno 2011). The majority of the studies discussed in this review performed recovery experiments by investigation of either spiked plant material or comparison of different analytical techniques to verify their results, revealing an accuracy ranging between ±5 and ±13 %.

However, all analytical methods are accompanied by advantages and disadvantages and have different limitations when considering complex real-world samples. These aspects are comprehensively summarized in an article written by *Schindl and Leopold* published in this book and are therefore not further discussed here.

1.2 Investigation of PGE Species-Specific Uptake

Information on species-specific uptake, accumulation and effects on plants can be obtained after exposure of plants with selected PGE species. For instance, barley plants were grown in nutrient solutions containing either Pd(II), Pd-NPs or micrometer-sizes silica-particles decorated with Pd-NPs (Leopold and Schuster 2010). As a result different uptake rates were observed, showing highest values for Pd-NPs exposed plants. Similar results were obtained for germination of Kiwi fruit pollen (Speranza et al. 2010). In both cases Pd-NPs were visualised by transmission electron microscopy (TEM) in pollen tubes and barley plant sap, respectively. However, TEM visualisation cannot be studied in collected outdoor plants, because considerably lower PGE concentrations occur in the plants and so the detection by electron microscopy techniques is almost impossible (Eybe et al. 2013).

1.3 Localisation of PGEs Within the Plants

Platinum group metals in plant tissues are typically detected by means of ICP-MS, ICP-OES, ETAAS or voltammetry after suitable sample preparation. For localisation of the PGE metals within a plant species separation of leaves, seeds and roots prior to measurement is mostly used. For instance, Mikulaskova et al. (2013) fractioned maize and pea plants into different subsamples by cutting the leaves and roots from the seed. After sample pre-treatment, the determination of PGE for each plant part could be achieved by adsorptive stripping differential pulse voltammetry. Highest concentrations were found in maize roots and shoots. The same trend was observed by Leopold and Schuster (2010) for barley plants exposed to Pd-NPs where highest Pd accumulation occurred in roots. Bonanno (2011) studied the distribution of PGE concentrations in roots, rhizomes, stems, and leaves of common reed collected at riverside in Sicily (Italy). They found a decreasing trend in element concentrations from root > rhizome > leaf > stem. Translocation factors were evaluated and revealed that Pt and Pd were mainly retained in roots, whereas Rh was mobile between roots and rhizomes, roots and stems, and roots and leaves. Kolodziej et al. (2007), investigating the Pt uptake in grass samples by voltammetric analysis, obtained similar results. Here, Pt contents in roots were much higher than in shoots. Several other investigations of plant collected in the field considered leaves (Pan et al. 2009; Fumagalli et al. 2010), roots, and shoots (Diehl and Gagnon 2007) separately. Typically, a PGE concentration gradient decreasing from roots > shoots > leaves > seeds was observed. However, since all these methods are destructive it is not possible to exactly localise the elements within the subsample, hence within the biological tissue. Electron beam techniques that could provide locally resolved information, like energy dispersive X-ray fluorescence or electron microscopy are however restricted to samples with (locally) high concentrations of the PGEs (Eybe et al. 2013). Therefore, this approach is only feasible for investigation of exposed plants, as shown by Speranza et al. (2010), who investigated Pd–NPs in germinated kiwifruit pollen by transmission electron microscopy (TEM). These TEM images revealed that 5–10 nm sized Pd-NPs were found in the cytoplasm or within vesicles.

2 Field Studies

2.1 Concentration Ranges in Plants

PGE concentrations in the environment have been increasing over the last 10 years within all investigated environmental compartments (Fig. 1). Several studies reveal that the PGE concentration in soil (Ribeiro et al. 2012), dust (Gao et al. 2012) and plants (Ayrault et al. 2006) in the vicinity of roads with heavy traffic often exceeds the natural background level by factors of 70–945. The PGE concentrations found in plant material sampled in the environment in recent years vary depending on the metal and plant species from 0.09 ng g^{-1} to 14.6 μg g^{-1} as summarized in Table 2.

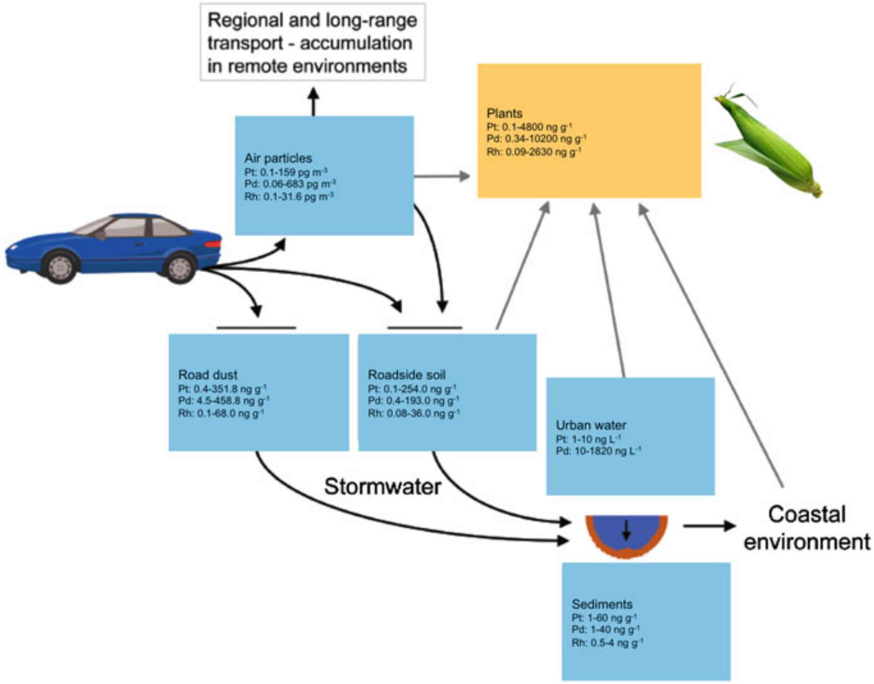

Fig. 1 Distribution pathways and concentration ranges of platinum group elements in selected environmental compartments. (Adapted from Rauch and Morrison (2008); Including values reported until 2013)

The most studied plants were grasses growing near roads as the most abundant vegetation in the vicinity of roads. They exhibit highest concentrations for platinum with values ranging from 1.44 to 256 ng g^{-1} (Rauch and Fatoki 2013; Pan et al. 2009). However, the maximum PGE content in a plant was detected in wild carrots. Diehl and Gagnon (2007) found 48 μg Pt g^{-1} in second year roots collected in Hyde Park (New York, USA). The plant morphology, here the big root, might be a reason for the high accumulation in μg g^{-1} range. In lichen and mosses relatively low concentrations were found, with a highest value of 3.31 ng Pt g^{-1} in moss (Niemelä et al. 2007). Due to their missing root system, they mostly rely on metal uptake from air components and are therefore excellent bioindicators of air pollution (Conti and Cecchetti 2001).

It is possible that some extremely high concentrations of PGE in plants reported in the past resulted from remaining contaminated dust on top of the collected plant material. Comparisons of washed and unwashed leaves sampled near a motorway showed higher contents of Pd and Rh in unwashed samples than in washed samples (Pan et al. 2009). Therefore, in order to exclude such artefacts, thorough and appropriate washing steps have to be included in the sample pretreatment procedure after collection of real samples. All work discussed here acknowledged this precondition.

Table 2 Typical concentration ranges of platinum, palladium and rhodium in plant material collected in the environment sorted by sampling site

PGE species	Vicinity of the collecting point	Plant species	Town country	PGE concentration in ng g^{-1} unless stated otherwise	References
Pd, Pt, Rh	Roads with high traffic density	Cocksfoot grass (*Dactylis glomeratus*)	Oxfordshire; London UK	Pd: 9.42 ± 4.96 Pt: 8.25 ± 6.47 Rh: 1.51 ± 0.71	Hooda et al. (2008)
				Pd: 3.78–23.75 Pt: 2.18–22.74 Rh: 0.64–3.89	
		Wild Carrot (*Daucus carota*)	Wappinger Falls; Southern Poughkeepsie; Northern Poughkeepsie; Hyde Park USA	Pd: 10–200 Pt: 4000–4800 Rh: 130–2630	Rose et al. (2010)
		Ryegrass (*Lolium perenne*)	The Plateau Lorrain France	Pd: 1.5–6.8 Pt: 0.3–1.4 Rh: 1.6–3	Tankari Dan-Badjo et al. (2007)
		Grass (family *Gramineae*)	Ionnina Greece	Pd: 1.1–2.2 Pt: 2.8–5.2 Rh: 1.8–24.5	Akrivi et al. (2012)
		Plant leaves near road	Guangzhou China	Pd: 0.77–1.77 Pt: 1.44–3.52 Rh: 0.14–1.16	Pan et al. (2009)
		Dandelions		Pd: 12.3 ± 10.6 Pt: 4.3 ± 3.1 Rh: 0.6 ± 0.4	Cyprien et al. (2008)
		Mosses		Pd: 27.6 ± 7.6 Pt: 14.1 ± 8.8 Rh: 1.2 ± 0.2	
		Ferns		Pd: 5.7 ± 2.3 Pt: 2.3 ± 0.4 Rh: 0.3 ± 0.1	
		Cherry laurel (*Prunus laurus cerasus*)	Varese Italy	Pd: 0.34–5.85 Pt: 0.11–2.05 Rh: 0.11–4.61	Fumagalli et al. (2010)
	Roads with low to medium traffic density	Ryegrass (*Lolium perenne*)	The Plateau Lorrain France	Pd: 10.6–17.3 Pt: 0.2–0.7	Tankari Dan-Badjo et al. (2008)

(continued)

Table 2 (continued)

PGE species	Vicinity of the collecting point	Plant species	Town country	PGE concentration in ng g^{-1} unless stated otherwise	References
				Rh: 1.5–1.9	
		Common reed (*Phragmites autralis*)	Licata (Sicily) Italy	Pd: <50–360 Pt: <50 Rh: 1100–1300	Bonanno (2011)
	Remote sites	Cherry laurel (*Prunus laurus cerasus*)	Varese Italy	Pd: 0.39–2.15 Pt: 0.11–0.47 Rh: 0.09–0.77	Fumagalli et al. (2010)
		Ryegrass (*Lolium perenne*)	The Plateau Lorrain France	Pd: 4.1 to 4.6 Pt: 0.6 to 1.2 Rh: 0.8 to 1	Tankari Dan-Badjo et al. (2007)
				Pd: 5.5 Pt: <0.25 Rh: 1.5	Tankari Dan-Badjo et al. (2008)
	Greenhouse	Ryegrass (*Lolium perenne*)	The Plateau Lorrain France	Pd: 3.5 Pt: <0.25 Rh: 1.7	Tankari Dan-Badjo et al. (2008)

(continued)

Table 2 (continued)

PGE species	Vicinity of the collecting point	Plant species	Town country	PGE concentration in ng g^{-1} unless stated otherwise	References
Pt, Rh	Roads with high traffic density	Moss (*Pleurozium schreberi*)	Helsinki; Riihimäki; Tampere; Jyväskylä; Oulu; Viitasaari; Jämsä; Ylikiiminki; Rovaniemi; Kuusamo; Sodankylä; Muonio; Puolanka; Salla Finland	Pt: <0.5–12.5 Rh: <0.2–4.5	Niemelä et al. (2007)
	Roads with low to medium traffic density			Pt: <0.5–5.67 Rh: <0.2–0.48	
	Roads with low to medium traffic density	Lichen (*Usnea barbata*)	Tierra del Fuego Argentina	Pt: 0.191–1.354 Rh: 0.336–0.663	Pino et al. (2010)
	Remote sites			Pt: 0.562–1.051 Rh: 0.264–0.340	
	Roads with high traffic density	Oleander (*Nerium oleander L.*)	Palermo Italy	Pt: 2–25 Rh: 1–5	Orecchio and Amorello (2010)
	Roads with low to medium traffic density			Pt: 0.1–2 Rh: 0.1–1.5	
	Remote sites			Pt: 0.1–1.5 Rh: <0.40	
	Industry			Pt: 1–2 Rh: <0.40	

(continued)

Table 2 (continued)

PGE species	Vicinity of the collecting point	Plant species	Town country	PGE concentration in ng g^{-1} unless stated otherwise	References
Pt	Roads with high traffic density	Grass	Upper Silesia Poland	Pt: 42–137	Kolodziej et al. (2007)
	Roads with low to medium traffic density			Pt: 19–59	
	Remote sites			Pt: 32–86	
	Industry	Grass (*Aristida bipartita*, *Bothriochloa insculpta*, *Digitaria eriantha*, *Ischaemum afrum*, *Panicum maximum*)	Bushveld Igneous Complex South Africa	Pt: 17–256	Rauch and Fatoki (2013)
	Roads with high traffic density	Holm-oak (Quercus ilex L.)	Caserta Italy	Pt: 100–2500	Papa et al. (2010)
	Remote sites			Pt: 100–300	

Anyway, it is clear that plants are able to take up metals by their root system from soil or water, but also from their leaves' surface. However, the mechanism of the latter uptake type is still unknown. The main uptake pathway of trace elements into plants is adsorption and uptake by roots (Kumar et al. 2006). Several studies showed that the highest PGE concentrations are generally found in the roots, followed by the shoots and the leaves (see Sect 1.3), indicating uptake but limited transport in the plants. Hence, PGEs mainly accumulate in roots and only a small fraction is transported into leaves. Accordingly, it is not suprising that highest concentrations of Pd (10.2 μg g^{-1}) and Pt (14.6 μg g^{-1}) were reported in wild carrots collected along a country highway with heavy traffic (Diehl and Gagnon 2007). For Rh, however, the highest value reported is about ten times lower (1.10 μg g^{-1}) and was detected in reed collected along a riverside affected by massive urbanisation (Bonanno 2011). In general only few research groups monitored Rh in plants, due to its lower abundance resulting from less applications. However, Rh was found to be the most soluble PGE in soil sorption studies, providing evidence for potentially high ecotoxicity of this element (Herincs et al. 2013). Comparing the concentrations of Pd, Pt and Rh in all plant material collected within the last 5 years in the environment, Pd concentrations were generally highest. Pd compounds are known to be more soluble and more mobile in the environment than Pt compounds and therefore show a presumably higher bioavailability (Moldovan et al. 2001). The mobility of PGEs in soils was studied for instance by Zereini et al. (2007), who found palladium even in a depth of about 12–16 cm in the ground near a German highway, while platinum and other noble metals stay near the surface. In addition, application of Pd as catalytic active metal in car exhaust converters has increased and exceeds the amount of Pt, since it is cheaper (Fumagalli et al. 2010; Moldovan et al. 2001). Orecchio and Amorello (2010) found a Pt/Rh concentration ratio of 4.8, which was in agreement with the typical mass ratio of these metals used in catalysts at the time. Comparing soil PGE concentration with plant PGE concentrations significant correlations could be found only for Pt and Rh, whereas grass Pd concentrations showed no relationship to the respective soil concentrations (Hooda et al. 2007). The examination of food samples purchased from retail outlets in selected towns of the UK, revealed Pt and Rh concentrations below the limit of detection (LOD) of 0.5 ng g^{-1} in all food groups, but palladium concentrations ranged between 0.23 ng g^{-1} in green vegetables and 1.9 ng g^{-1} in nuts. However, Pd contents in fresh fruits were below the LOD of 0.03 ng g^{-1} (Rose et al. 2010).

2.2 *Sampling Sites*

Analyses of plants originating from different locations can provide valuable information on the source and extent of PGE emission as well as on transport and fate of PGEs in urban environments. Thereby, the description of the area of sampling, including roadside distance, average traffic, and even weather conditions is important. As shown in many studies, urban areas are recognized to be major sources and sinks for contaminations, because here several activities lead to elevated emissions of contaminants (Diamond and Hodge 2007; Markert et al. 2011). The level of PGE concentrations in urban environments in developed and developing countries has considerably increased within the last decades and the spread of these elements is becoming rapid and wide with the broad application of catalyst converters. Biomonitoring traffic-related Pt and Rh deposition on terrestrial moss in Finland revealed higher element concentrations for urban areas with high traffic densities compared to the countryside with medium to low traffic density (Niemelä et al. 2007). Elevated Pt concentrations were observed in the vicinity of Pt mines as well as in towns within a few kilometres of a smelter, where the highest Pt value was found (Rauch and Fatoki 2013). Furthermore, lower Pt values of 0.33 $\mu g\ kg^{-1}$ were found in rural italian areas and higher Pt values of 25 $\mu g\ kg^{-1}$ in the city centre of Palermo (Italy) (Orecchio and Amorello 2010). Investigations of Fumagalli et al. (2010) show five to ten times higher PGE levels for locations along urban sections than in the surrounding area.

Within urban areas the distribution of PGE concentration depends mainly on traffic fluxes and road types. Highest concentrations are expected in areas with high traffic density and /or high-speed roads, whereas in residential areas fewer amounts of PGEs accumulate. This trend could be observed by Kolodziej et al. (2007) with highest Pt contents in grass samples collected in the vicinity of a motorway and lowest in plants near park lanes. In contrast to the assumption that in areas with frequent stop-start behaviour higher PGE values are expected, Akrivi et al. (2012) identified that grass located close to low speed roads with stop/start cycles accumulate less PGEs.

Another aspect that has to be accounted for when considering site-depending contamination is the size of the particles that are emitted. Whereas relatively large particles are expected to deposit close to their source, i.e. beside roads, a significant fraction of particles containing PGE in automobile emissions has a sufficiently long atmospheric residence time to be transported over long distances (Rauch et al. 2005). A few studies dealing with alpine snow and remote Greenland snow indicate that PGEs can be transported at ultra trace levels even to remote areas (Van de Velde et al. 2000; Barbante et al. 2001). Of course wind direction and wind speed was shown to have an influence on PGE concentration in grasses and soils (Schäfer and Puchelt 1998). Comparing the Pd content in ryegrass collected at the north and south side of a road, higher concentrations were found at the north side due to the effect of the wind coming from southwest. In this regard, most studies confirm again, that palladium in comparison to other platinum group metals shows the highest mobility in the environment. In the study of Tankari Dan-Badjo et al. (2008), for instance, platinum could only be detected in grass samples grown at the road site, whereas Pd and Rh was found in plants collected along the road as well as in isolated pastures and greenhouses.

2.3 Seasonality

As shown before, weather conditions can affect the content of the metals in plant samples. Only few studies are dealing with the influence of seasonal climate changes. Sampling in 3-month intervals in summer, autumn, winter and spring revealed higher PGE concentrations during spring and summer and lower during autumn and winter, reflecting the seasonal changes of Mediterranean climate with dry, hot summers and rainy, bland winters (Akrivi et al. 2012). Furthermore, Fumagalli et al. (2010) sampled cherry laurel leaves monthly in October 2004–May 2005 and January–September 2007 in the city of Varese. Here, highest platinum, palladium and rhodium concentrations were observed in the unusually dry period of January–April and July 2007. Heavy rains in May, August and September led to significant lower PGE values. In contrast, results of Papa et al. (2010) investigating platinum at the beginning and the end of seasonal vegetation cycles in the leaves of holm-oak, showed highest concentrations in autumn 2004 with the most abundant rainfall recorded during the investigation.

3 Exposure Experiments

The investigation of PGE contents in plants collected in the environment revealed very low concentrations in ng g^{-1} range. In order to study uptake mechanisms, translocation, toxic effects or to determine the PGE species, several researchers carried out exposure studies using higher PGE concentrations.

3.1 Types of Exposure Studies

In order to assess possible risks arising from PGEs, several ways of PGE exposure have been investigated in plant studies within the last 5 years. However, most exposure studies were performed with one individual species/form rather than comparative studies using several species/forms. Often ionic species, i.e. salts of platinum group metals were used in order to study general uptake mechanisms, accumulation and effects of PGEs (Odjegba et al. 2007). In this regard, the ability of the metal ions to form complexes with compounds present in water and soil plays an important role for the bioavailability and uptake. After cultivation of *Elodea canadensis* in 0.1 mg Pt(IV) L^{-1} at pH 8 higher Pt uptake was detected when humic acids were added (Diehl and Gagnon 2007). Moreover, the impact of the metals on the uptake and use of essential mineral nutrients were examined (Diehl and Gagnon 2007). Similar to this intention the change in the content of amino acids, thiol and phytochelatin synthase activity, products in metal detoxification mechanisms of plants, were determined in plants exposed to Pt(IV) species (Mikulaskova et al. 2013).

However, the chemical form of the PGE is of great interest as it may substancially influence uptake and accumulation.

Under environmental conditions, PGEs undergo rapid transformation to a variety of species such as colloidal PGE species, cationic and anionic chloro and hydroxo complexes, humic acid complexes etc. These effects can be mimicked when using e.g. ground car catalyst material for bioavailability/uptake studies. However, this strategy suffers from the problem, that only the surface of the ceramic monolith material used in typical car exhaust catalysts contains the catalytically active PGE particles, whereas the bulk material mainly consists of oxides of aluminium, silicon, magnesium, and cerium (Martin et al. 2003). The bulk material also may contain toxic compounds resulting from the combustion process (oil residues, additives etc.) or engine abrasion material, which may interfere with PGE-related biological effects. The use of original road dust guarantees an exposure form with environmental relevant PGE species, but the biological effects arising with this kind of exposure may be overlapped by other traffic-emitted heavy metals such as Pb, Zn, Cd, and Cu (Schäfer et al. 1998). In this regard, studies with PGE material similar to the species released into and the species that are probably formed in the environment are required. In conclusion, exposure experiments should simulate the conditions actually occuring in the environment in the best possible way without compromising the observable effects in order to reflect the real situation most properly.

For palladium such an approach was applied to study the uptake and toxic effects of traffic-related Pd emissions on barley (Battke et al. 2008) and kiwifruit pollen (Speranza et al. 2010). Here, test materials, i.e. Pd nanoparticles, micrometer-sized Pd particles and silica supported Pd nanoparticles, were synthesised in order to mimick traffic-related palladium emission (Leopold and Schuster 2010). A comparison of Pd(II) exposure to Pd-NPs exposure of kiwifruit pollen revealed significant differences in germination (Speranza et al. 2010). Moreover, comparing the uptake of Pd nanoparticles and micrometer-sized Pd particles showed 5- to 15-fold higher Pd content in barley plants for nanoparticle exposed plants. Here, the small nanoparticles could enter the xylem via the cortex and the central cylinder, whereas larger particles are too big for direct uptake via roots and/or conduction in the xylem, resulting in lower accumulation (Faiyue et al. 2010). Silica supported Pd nanoparticles, which are similar to particles released by catalytic converters, show even lower contents in barley plants (Leopold and Schuster 2010).

3.2 Metal Uptake Rates and Localisation

Most exposure studies apply exposure concentrations in the mg L^{-1} level, ranging from 0.05 mg L^{-1} (e.g. Diehl and Gagnon 2007) to 160 mg L^{-1} (e.g. Supalkova et al. 2008). Concentration dependent experiments typically reveal, as expected, increasing PGE contents in the plants with higher exposure concentrations (see e.g. Diehl and Gagnon 2007; Leopold and Schuster 2010; Supalkova et al. 2008;

Mikulaskova et al. 2013). Nevertheless, Supalkova et al. (2008) observed a decrease of cisplatin content at the third and fourth day of cultivation due to affected DNA replication and increase synthesis of thiols, a protection mechanism of plants, caused by cisplatin. Table 3 provides an overview of PGE concentrations that have been measured in plant materials received from exposed cultivation under different conditions. When considering the ratio of PGE content found in dry biomass to concentration in exposure media, uptake rates range from 2 to 400 for Pd, 54 to 800 for Pt and 55 to 1200 for Rh (Odjegba et al. 2007; Nischkauer et al. 2013; Diehl and Gagnon 2007). This finding seems on the first glance contradictory to the concentrations of Rh, Pt and Pd found in plants in field studies, where Pd was found in highest concentrations among the PGE. However, Rh concentrations in soils and sediments are significantly lower than those for Pd or Pt. Moreover, PGEs undergo a rapid transformation in the environment, in which substances like e.g. humic acids may influence substancially their solubility and mobility, hence their bioavailability (Diehl and Gagnon 2007; Zimmerman et al. 2003).

Regarding localisation of PGE, accumulation takes places first of all in vegetative parts of plants and decrease in the following order: roots, stalks, leaves. In leaves of *Peltandra virginica* even no PGEs could be detected, indicating the lack of translocation to aerial plant parts (Diehl and Gagnon 2007). These results are in perfect agreement with observation made in plants collected in field studies.

3.3 Observed Effects

Obviously, biological effects observed in exposure studies were found to be highly dependent on the PGE concentration in the nutrient media. Observable effects typically occurred at low mg L^{-1} levels (regarding exposure concentrations). General effects were decreases in germination rate of plant seeds, biomass production and chlorophyll concentration in leaves. These effects occured at exposure concentrations of 0.7 mg L^{-1} for exposure with Rh, Pd or Pt compounds (Odjegba et al. 2007). This concentration is not much higher than the values presently detected at contaminated sites in the environment for the three metals (soils: 0.5–500 μg kg^{-1} see chapter on "Analysis of Platinum Group Elements in Environmental Samples: A Review" this book). However, it has to be considered that the Pt, Pd and Rh concentrations found in soils are a sum of all species of one element (i.e. chemical forms), whereas the bioavailable concentration is obviously lower. Comparing the different exposure forms/species of PGE most distinct effects were observed for exposure with particulate Pd. Palladium nanoparticles significantly affected the pollen tube emergence at exposure concentrations of only 0. 1 mg L^{-1} and led to complete cessation at exposure concentrations of 0.4 mg L^{-1}, while Pd(II) chloride toxicity was observable only at elevated levels (2.5 mg Pd L^{-1}) (Speranza et al. 2010). The cells of kiwifruit pollen showed wrinkled morphology and cell aggregation with increasing Pd-NP exposure concentration and time (Speranza et al. 2010). Strongest effects on plant growth were

Table 3 Summary of reported exposure studies for platinum, palladium and rhodium to different plant species within the last 5 years

Exposed PGE species/form	Plant species	Cultivation conditions	Exposure concentrations in mg L^{-1} unless stated otherwise	Detected PGE concentrations in μg g^{-1} unless stated otherwise	Reference
$PdCl_2$	Canadian water-weed (*Elodea canadensis*)	Growth in climate chamber; Exposure for 2 weeks; Sigma bold modified basal nutrient solution; Addition of humic acid or Ca $(NO_3)_2$	0.1	Pd: <detection limit (NA)	Diehl and Gagnon (2007)
	Green arrow arum (*Peltandra virginica*)				
	Lettuce	Growth in climate chamber; Exposure for 6 weeks; Hoagland's nutrient solution (pH 6.5); Replacement of PGE solutions every 5 days	0.3, 0.5, 0.7, 1.0	Pd: 5–28	Odjegba et al. (2007)
	Kiwifruit pollen (*Actinidia deliciosa var. deliciosa*)	Pre-cultivation for 30 min; Growth in climate chamber; Exposure for 30 or 90 min; Basal medium containing sucrose and H_3BO_3	0.25, 0.5, 1, 2.5, 5.0, 7.0	Pd: 20–530	Speranza et al. (2010)
Pd-NPs	Barley (*Hordeum vulgare L.*)	Growth in climate chamber; Exposure for 1 week; Hoagland's media (5 %)	1, 2, 4, 6, 8, 10, 20, 30, 40, 50 μmol L^{-1}	Pd: 5–325	Battke et al. (2008)
		Growth in climate chamber; Exposure for 2 weeks; Hoagland's media (5 %)	1.1, 2.7, 5.3, 8.0, 10.6	Pd: 10–1000	Leopold and Schuster (2010)
	Kiwifruit pollen (*Actinidia deliciosa var. deliciosa*)	Pre-cultivation for 30 min; Growth in climate chamber; Exposure for 30 or 90 min; Basal medium containing sucrose and H_3BO_3	0.25, 0.5, 1, 2.5 and 7	Pd: 0.2–95 mg g−1	Speranza et al. (2010)

(continued)

Table 3 (continued)

Exposed PGE species/form	Plant species	Cultivation conditions	Exposure concentrations in mg L^{-1} unless stated otherwise	Detected PGE concentrations in μg g^{-1} unless stated otherwise	Reference
Pd micrometer-sized particles	Barley (*Hordeum vulgare L.*)	Growth in climate chamber; Exposure for 1 week; Hoagland's media (5 %)	1, 2, 4, 6, 8, 10, 20, 30, 40, 50 μmol L^{-1}	Pd: 0.2–17	Battke et al. (2008)
		Growth in climate chamber; Exposure for 2 weeks; Hoagland's media (5 %)	1.1, 2.7, 5.3, 8.0, 10.6 μmol L^{-1}	Pd: 1–700	Leopold and Schuster (2010)
Pd-NPs entrapped in aluminium hydroxide matrix	Lettuce	Exposure for 11 days; Potting mix (6.2 % (w/w)	0.013 % (w/w), 0.066 % (w/w)	NA	Shah and Belozerova (2009)
Pd-NPs/SiO_2	Barley (*Hordeum vulgare L.*)	Growth in climate chamber; Exposure for 2 weeks; Hoagland's media (5 %)	1.1, 2.7, 5.3, 8.0, 10.6 μmol L^{-1}	Pd: 1–400	Leopold and Schuster (2010)
$Pd(NO_3)_2$	Rapeseed (*Brassica napus*)	Germination for 5 days; Pre-cultivation for 4 weeks; Exposure for 4 weeks	0.5, 1.0	Pd: <0.16–200	Nischkauer et al. (2013)

(continued)

Table 3 (continued)

Exposed PGE species/form	Plant species	Cultivation conditions	Exposure concentrations in mg L^{-1} unless stated otherwise	Detected PGE concentrations in µg g^{-1} unless stated otherwise	Reference
$H_2[PtCl_6]$ $*6H_2O$	Canadian waterweed (*Elodea canadensis*)	Growth in climate chamber; Exposure for 2 weeks; Sigma Bold Modified Basal Nutrient Solution (pH = 5, 6, 7 or 8); pH adjustment with NaOH or HCl; Addition of humic acid, $Ca(NO_3)_2$, or $ZnCl_2$	0.05, 0.1, 1.0, 5.0	Pt: 6.4–1628.4	Diehl and Gagnon (2007)
	Green arrow arum (*Peltandra virginica*)			Pt: 5.5–13.2	
	Lettuce	Growth in climate chamber; Exposure for 6 weeks; Hoagland's nutrient solution (pH 6.5); Replacement of PGE solutions every 5 days	0, 0.3, 0.5, 0.7, 1.0	Pt: 14–54	Odjegba et al. (2007)
Pt $(NH_3)_4(NO_3)_2$	Lucerne (*Medicago sativa*)	Germination for 48 h; Growth for 3 weeks in Hoagland's media; Growth in climate chamber; Exposure for 24, 48, or 72 h; Hoagland's nutrient solution (pH 2, 3, 5, 7 or 9)	5, 10, 20, 40, 80	Pt: 20–94190	Bali et al. (2010)
	Brown mustard (*Brassica juncea*)			Pt: 20–24400	
	Rapeseed (*Brassica napus*)	Germination for 5 days; Pre-cultivation for 4 weeks; Exposure for 4 weeks	0.5, 1.0	Pt: 100–400	Nischkauer et al. (2013)
$PtCl_4$	Maize (*Zea mays L.*)	Growth in cultivation box; Exposure for 8 and 12 days	5, 10, 25, 50, 100 µmol L^{-1}	Pt: 0.25–100 µM	Mikulaskova et al. (2013)
	Pea (*Pisum sativum L.*)			Pt: 0.05–100 µM	

(continued)

Table 3 (continued)

Exposed PGE species/form	Plant species	Cultivation conditions	Exposure concentrations in mg L^{-1} unless stated otherwise	Detected PGE concentrations in µg g^{-1} unless stated otherwise	Reference
Cisplatin	Lesser duckweed (*Lemna minor*)	Pre-cultivation for 2 weeks; Growth in climate chamber; Exposure for 4 days; Diluted nutrient solution of SIS	5, 10, 20, 40, 80, 160 µmol L^{-1}	Pt: 0.01–0.35	Supalkova et al. (2008)
$RhCl_3$	Canadian waterweed (*Elodea canadensis*)	Growth in climate chamber; Exposure for 2 weeks; Sigma Bold Modified Basal Nutrient Solution; Addition of humic acid or Ca $(NO_3)_2$	0.1	Rh: 45–96.2	Diehl and Gagnon (2007)
	Green arrow arum (*Peltandra virginica*)			Rh: 22.6–96.2	
	Lettuce	Growth in climate chamber; Exposure for 6 weeks; Hoagland’s nutrient solution (pH 6.5); Replacement of PGE solutions every 5 days	0.3, 0.5, 0.7, 1.0	Rh: 12–55	Odjegba et al. (2007)
	Rapeseed (*Brassica napus*)	Germination for 5 days; Pre-cultivation for 4 weeks; Exposure for 4 weeks	0.5, 1.0	Rh: 1–600	Nischkauer et al. (2013)

caused by Pd-NPs entrapped in an aluminium hydroxide matrix (Shah and Belozerova 2009). However, the observed effects do not necessarily arise from the uptake of Pd, but aluminium hydroxide is suspected to affect the biological reaction of the plants (Schäfer et al. 1998).

4 Conclusions and Outlook

The determination of platinum group elements (PGEs) such as platinum, palladium and rhodium in plant samples within the last years confirmed the increased contamination of urban sites with these metals. Considering the results from several exposure experiments in combination with monitoring studies of PGEs in plants collected from the field suggest that differences in the mobility and transformation behaviour of the three elements, Pt, Pd and Rh in the environment are significant for their bioavailability. Exposure studies reveal that uptake rates are highest for Rh followed by Pt and lowest for Pd. However, from field studies we know that Pd accumulation in plants is most distinct. Even in vegetarian food samples and pastures Pd was detected clearly above background levels. Hence, further monitoring studies should reveal whether the increase in accumulation will continue and which effects are to be expected concerning ecological consequences, the food chain and human health. In order to enhance the reliability of collected data in the future it seems important to define suitable standard procedures for analytical validation (e.g. certified reference material, standard methods for comparison, etc.) and exposure studies (exposure species, test materials with isolated or combined PGEs species).

References

Akrivi AA, Tsogas GZ, Giokas DL, Vlessidis AG (2012) Analytical determination and biomonitoring of platinum group elements in roadside grass using microwave assisted digestion and electrothermal atomic absorption spectrometry. Anal Lett 45:526–538

Ayrault S, Li C, Gaudry A (2006) Biomonitoring of Pt and Pd in mosses. Palladium emissions in the environment: analytical methods, environmental assessment and health effects. Springer, Berlin, pp 525–536

Bali R, Siegele R, Harris AT (2010) Biogenic Pt uptake and nanoparticle formation in *Medicago sativa* and *Brassica juncea*. J Nanopart Res 12:3087–3095

Barbante C, Vesseyre A, Ferrari C, Van de Velde K, Morel C, Capodaglio G, Cescon P, Scarponi G, Boutron C (2001) Greenland snow evidence of large scale atmospheric contamination for platinum, palladium and rhodium. Environ Sci Technol 35:835–839

Battke F, Leopold K, Maier M, Schmidhalter U, Schuster M (2008) Palladium exposure of barley: uptake and effects. Plant Biol 10:272–276

Bencs L, Ravindra R, Van Grieken R (2003) Methods for the determination of platinum group elements originating from the abrasion of automotive catalytic converters. Spectrochim Acta Part B 58:1723–1755

Bonanno G (2011) Trace element accumulation and distribution in the organs of *Phragmited australis* (common reed) and biomonitoring applications. Ecotox Environ Safe 74:1057–1064

Bosch Ojeda C, Sánchez Rojas F, Cano Pavón JM (2007) On-line preconcentration of palladium (II) using a microcolumn packed with a chelating resin, and its subsequent determination by graphite furnace atomic absorption spectrometry. Microchim Acta 158:103–110

Conti ME, Cecchetti G (2001) Biological monitoring: lichens as bioindicators of air pollution assessment. Environ Poll 114:471–492

Cyprien M, Barbaste M, Masson P (2008) Comparison of open digestion methods and selection of internal standards for the determination of Rh, Pd and Pt in plant samples by ICP-MS. Intern J Environ Anal Chem 88:525–537

Diamond M, Hodge E (2007) Urban contaminant dynamics: from source to effect. Environ Sci Technol 541:3796–3805

Diehl DB, Gagnon ZE (2007) Interactions between essential nutrients with platinum group metals in submerged aquatic and emergent plants. Water Air Soil Pollut 184:255–267

Eybe T, Audinot J-N, Udelhoven T, Lentzen E, El Adib B, Ziebel J, Hoffmann L, Bohn T (2013) Determination of oral uptake and distribution of platinum and chromium by the garden snail (*Helix aspersa*) employing nano-secondary ion mass spectrometry. Chemosphere 90:1829–1838

Faiyue B, Al-Azzawi MJ, Flowers TJ (2010) The role of lateral roots in bypass flow in rice (*Oryza sativa L*). Plant Cell Environ 33:702–716

Fumagalli A, Faggion B, Ronchini M, Terzaghi G, Lanfranchi M, Chirico N, Cherchi L (2010) Platinum, palladium, and rhodium deposition to the *Prunus laurus cerasus* leaf surface as an indicator of the vehicular traffic pollution in the city of Varese area. Environ Sci Pollut Res 17:665–673

Gao B, Yu Y, Zhou H, Lu J (2012) Accumulation and distribution characteristics of platinum group elements in roadside dusts in Beijing, China. Environ Tox Chem 31:1231–1238

Georgieva M, Pilar B (1997) Determination of anthropogenic input of Ru, Rh, Pd, Re, Os, Ir and Pt in soils along Austrian motorways by isotope dilution ICP-MS. Sci Total Environ 325:145–154

Haus N, Eybe T, Zimmermann S, Sures B (2009) Is microwave assisted digestion a suitable preparation method for Pt determination in biological samples by adsorptive cathodic stripping voltammetry (ACSV)? Anal Chim Acta 635:53–57

Herincs E, Puschenreiter M, Wenzel W, Limbeck A (2013) A novel flow-injection method for simultaneous measurement of platinum (Pt), palldium (Pd) and rhodium (Rh) in aqueous soil extracts of contaminated soil by ICP-OES. J Anal At Spectrom 28:354–363

Hooda PS, Miller A, Edwards AC (2007) The distribution of automobile catalysts-cast platinum, palladium and rhodium in soils adjacent to roads and their uptake by grass. Sci Total Environ 384:384–392

Hooda PS, Miller A, Edwards AC (2008) The plant availability of auto-cast platinum elements. Environ Geochem Health 30:135–139

Kolodziej M, Baranowska I, Matyja A (2007) Determination of platinum in plant samples by voltammetric analysis. Electroanalysis 19:1585–1589

Kumar NJI, Soni H, Kumar RN (2006) Biomonitoring of selected freshwater macrophytes to assess trace element contamination: A case study of Nal Sarovar Bird Sanctuary, Gujarat, India. J Limnol 65:9–16

Leopold K, Schuster M (2010) Urban airborne particulate matter, environmental science and engineering. In: Pd particles as standardized test material for bioavailability studies of traffic related Pd emissions to barley plants. Springer, Berlin, pp 399–410

Markert B, Wünschmann S, Fränzle S, Graciana Figuereido AM, Ribeirao A, Wang M (2011) Bioindication of atmospheric trace metals-with special reference to megacities. Environ Poll 159:1991–1995

Martin L, Arranz JL, Prieto O, Trujillano R, Holgado MJ, Galan MA, Rives V (2003) Simulation three-way catalyst ageing: analysis of two conventional catalyst. Appl Catal B Environ 44:41–52

Mikulaskova H, Merlos MAR, Zitka O, Kominkova M, Hynek D, Adam V, Beklova M, Kizek R (2013) Employment of electrochemical methods for assessment of the maize (*Zea mays L.*) and pea (*Pisum sativum L.*) response to treatment with platinum (IV). Int J Electrochem Sci 8:4505–4519

Moldovan M (2007) Origin and fate of platinum group elements in the environment. Anal Bianal Chem 388:537–540

Moldovan M, Rauch S, Gómez M, Palacios MA, Morrison GM (2001) Bioaccumulation of palladium, platinum and rhodium from urban particulates and sediments by the freshwater isopod *Asellus aquaticus*. Water Res 35:4175–4183

Niemelä M, Piispanen J, Poikalainen J, Perämäki P (2007) Preliminary study of the use of terrestrial moss (*Pleurozium schreberi*) for biomonitoring traffic-related Pt and Rh deposition. Arch Environ Contam Toxicol 52:347–354

Nischkauer W, Herincs E, Puschenreiter M, Wenzel W, Limbeck A (2013) Determination of Pt, Pd and Rh in *Brassica Napus* using solid sampling electrothermal vaporization inductively coupled plasma optical emission spectrometry. Spectrochim Acta Part B 89:60–65

Odjegba VJ, Brown MT, Turner A (2007) Studies on the effects of platinum group elements on *Lactuca sativa L.* Am J Plant Physiol 3:183–194

Orecchio S, Amorello D (2010) Platinum and rhodium associated with the leaves of *Nerium oleander L.*; analytical method using voltammetry; assessment of air quality in the Palermo (Italy) area. J Hazard Mater 174:720–727

Pan S, Zhang G, Sun Y, Chakraborty P (2009) Accumulating characteristics of platinum group elements (PGE) in urban environments, China. Sci Total Environ 407:4248–4252

Papa S, Bartoli G, Di Martino D, Fioretto A (2010) Occurence of platinum in the leaves of holm-oak (*Quercus ilex L.*) from different sites (streets and squares) in the city of Caserta (Italy). Fresen Environ Bull 19:2109–2115

Pino A, Alimonti A, Conti ME, Bocca B (2010) Iridium, platinum and rhodium baseline concentration in lichens from Tierra del Fuego (South Patagonia, Argentina). J Environ Monitor 2:1857–1863

Rauch S, Hemond HF, Barbante C, Owari M, Morrison GM, Peucker-Ehrenbrink B, Wass U (2005) Importance of automobile exhaust catalyst emission for the deposition of platinum, palladium, and rhodium in the northern hemisphere. Environ Sci Technol 39:8156–8162

Rauch S, Morrison GM (2008) Environmental relevance of the platinum-group elements. Elements 4:259–263

Rauch S, Fatoki OS (2013) Anthropogenic platinum enrichment in the vicinity of mines in the Bushveld Igneous Complex, South Africa. Water Air Soil Pollut 224:1395–1403

Ribeiro AP, Figueiredo AMG, Sarkis JES, Hortellani MA, Markert B (2012) First study on anthropogenic Pt, Pd, and Rh levels in soils from major avenues of Sao Paulo City. Brasil Environ Monit Assess 184:7373–7382

Rose M, Baxter M, Brereton N, Baskaran C (2010) Dietary exposure to metals and other elements in the 2006 UK Total Diet Study and some trends over the last 30 years. Food Addit Contam 27:1380–1404

Sánchez Rojas F, Bosch Ojeda C, Cano Pavón JM (2009) Simultaneous determination of palladium and rhodium using on-line column enrichment and electrothermal atomic absorption spectrometric detection. J Anal Chem 64:241–246

Schäfer J, Puchelt H (1998) Platinum-group metals (PGM) emitted from automobile catalytic converters and their distribution in roadside soils. J Geochem Explor 64:307–314

Schäfer J, Hannker SD, Eckhardt JD, Stüben D (1998) Uptake of traffic-related heavy metals and platinum group elements PGE by plants. Sci Total Environ 215:59–67

Shah V, Belozerova I (2009) Influence of metal nanoparticles on the soil microbial community and germination of lettuce seeds. Water Air Soil Pollut 197:143–148

Speranza A, Leopold K, Maier M, Taddei AT, Scoccianti V (2010) Pd-nanoparticles cause increased toxicity to kiwifruit pollen compared to soluble Pd(II). Environ Pollut 158:873–882

Supalkova V, Beklova M, Baloun J, Singer C, Sures B, Adam V, Huska D, Pikula J, Rauscherova L, Havel L, Zehnalek J, Kizek R (2008) Affecting of aquatic vascular plant *Lemna Minor* by cisplatin revealed by voltammetry. Bioelectrochemistry 72:59–65

Tankari Dan-Badjo A, Ducoulombier-Crépineau C, Soligot C, Feidt C, Rychen G (2007) Deposition of platinum group elements and polycyclic aromatic hydrocarbons on ryegrass exposed to vehicular traffic. Agron Sustain Dev 27:261–266

Tankari Dan-Badjo A, Rychen G, Ducoulombier C (2008) Pollution maps of grass contamination by platinum group elements and polycyclic aromatic hydrocarbons from road traffic. Agron Sustain Dev 28:457–464

Van de Velde K, Barbante C, Cozzi G, Moret I, Bellomi T, Ferrari C, Boutron C (2000) Changes in the occurence of silver, gold, platinum, palladium and rhodium in Mont Blanc ice and snow since the 18th century. Atmos Environ 34:3117–3127

Zereini F, Wiseman C, Püttmann W (2007) Changes in palladium, platinum and rhodium concentrations and their spatial distribution in soils along a major highway in Germany from 1994 to 2004. Environ Sci Technol 41:451–456

Zimmerman S, Menzel CM, Stüben D, Taraschewski H, Sures B (2003) Lipid solubility of the platinum group metals Pt, Pd and Rh in dependence on the presence of complexing agents. Environ Poll 124:1–5

Monitoring of Platinum Group Element Deposition by Bryophytes

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Abstract At first the book chapter gives a short introduction in the mechanism of uptake and retention of PGEs by bryophytes. Two general methods of biomonitoring (active and passive methods) are described by short examples. An extensive description of the analysis of moss material is given and pitfalls within the analytical process are highlighted. A series of examples and results from monitoring of PGEs by bryophytes are given, however the range of application is rather small up to date. Results from background areas, traffic sites and urban/industrial sites are show, ranging from 0.01 ng Pt/g dryweight in remote areas to 41.5 ng Pt/g dryweight in a traffic tunnel. Only in a few studies Pd and Rh were analysed too. The moss method is comparable credible and cheap in costs and probably the best biomonitoring method for the detection of atmspheric PGE deposition.

Keywords Background values · Bryophytes · Pt · Pd · Rh · Traffic

1 Introduction

The use of organisms for monitoring environmental pollution, also called biomonitoring, has developed indispensable methods for the assessment of environmental pollution and ecosystem health (Markert et al. 2003). Bryophytes have been used as biomonitors for heavy metal deposition for three decades (Zechmeister et al. 2003;

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Harmens et al. 2012). Bryophytes represent autotrophic cryptogams classified into four clades which developed in the early stage of onshore occupation. Mosses are the by far largest group within bryophytes. Up to date about 10,000 species are known on a worldwide level. Mosses are generally short (less than 1 cm) but some can grow up to a length of 70 cm (e.g. *Polytrichum, Dawsonia*). In contrast to vascular plants they rarely grow as single stems but in groups forming turfs, cushions, wefts or other growth forms. Mosses show a limited range of anatomical or morphological features but a wide range of physiological and dispersal adaptations to stress caused by natural or anthropogenic disturbance (e.g. Bates and Farmer 1992; Vanderpoorten and Goffinet 2009).

Mosses thrive in humid climates, but can be found all over the world, even in arid regions. As a consequence to slow evolution many dominant species can be found all over the world, or show at least a circumpolar distribution. They colonise nearly every kind of terrestrial substrate and a wide range of species grows in areas unable to be colonised by any other plant (e.g. Smith 1983), which is significant for many aspects in biomonitoring.

The use of mosses in an increasing number of monitoring programs is based on a wide range of remarkable anatomical and physiological properties, which are briefly reviewed:

Mosses are built up by only one cell layer so the surface/volume ratio is high, additionally there is no continuous water-repellent cuticle. In consequence most bryophytes receive water as well as mineral nutrients predominantly by atmospheric depositions. Only a few species (e.g. *Polytrichum* ssp.) obtain additional water and soluble nutrients from the substrate (Glime 2009).

Elements trapped by bryophytes can be attributed to four possible locations (Brown and Bates 1990; Bates 1992): trapped particulate matter, extracellular bound to cell wall on charged exchange sites, intracellular and intercellular soluble. Particulate matter and intercellular elements are unbound ions in the water free space and can easily be removed by washing or mechanic treatment. Exchangeable cations are bound to positively charged exchange properties of the cell wall and are fixed by a process mainly depending on physico-chemical processes and are not physiologically active, whereas intracellular elements fulfil a physiological function. By far the largest amount of trapped elements is fixed in the extracellular matrix and bound by cationic exchange capacities of non-esterified polyuronic acid molecules (e.g. Sari et al. 2009). Popper and Fry (2003) have demonstrated that mosses have higher concentrations of glucuronic acid in their cell walls than any other land plants. Binding conforms to strict physical and chemicals rules. External uptake is rapid and occurs within the first few minutes during rainfall (Gjengedahl and Steinnes 1990). The uptake depends on the nature of the elements only, irrespective of the physiological condition of the plant. Monovalent cations show less affinity than polyvalent metals. The uptake of heavy metals is only slightly influenced by pH of the precipitation and air temperature. The total metal binding is determined by the number of available exchange sites and morphological structures of the mosses, which differs slightly from species to species. Binding capacities are much higher than deposition under natural conditions therefore the accumulation is constant over the overall growth period. One should keep in mind that the uptake and therefore concentration in moss is linear to the deposition of elements under natural conditions and bryophytes do not enrich certain elements. Due to long accumulation periods concentrations are often higher than in bulk samplers and therefore analytical procedures show higher validity (Zechmeister et al. 2003). According to their unique uptake mechanism mosses show comparable higher concentrations than most other plant material, e.g. grasses, flowering plants, needles or bark (Djingova et al. 2003; Cyprien et al. 2008).

Younger parts of the plants show higher amounts of monovalent cations and nutrient anions than older parts. Divalent cations, especially heavy metals, show the reverse distribution. Dead tissues retain polyvalent cations more effectively still (Ruhling and Tyler 1970; Pakarinen and Rinne 1979). Therefore, only green parts of the moss are used in most biomonitoring studies. Bryophyte species used for biomonitoring studies have a life span lasting for several years. As decomposition is slow for bryophytes green parts of the pants have mostly an age of three or more years. For several species (e.g. *Hylocomium splendens, Pleurozium schreberi, A-bietinella abietina*; see also Zechmeister 1998) the age of these parts can be defined exactly. By analysing these green parts one get information of the deposition in a clearly defined time period. A single collection of adequate moss can replace a multiple measurement by technical equipment. This is one more outstanding feature of biomonitoring by bryophytes.

Cost efficiency is another added value of monitoring by bryophytes. Due to continuous uptake of pollutants a single sampling procedure can replace repeated measurements.

Two methods have been used for using mosses as monitors of metals incl. PGEs. By *"active monitoring"* mosses were collected in background areas and exposed in the targeted monitoring sites. Before exposure mosses were mostly washed in double distilled water to remove adhering particles and get an even distribution of the background level in the extracellular matrix. After drying mosses were exposed in wooden frames with the moss covered by a fine mesh (e.g. Zechmeister et al. 2006a). The method using frames has the advantage of a high surface and a more even distribution of the elements in the moss matrix. After a defined exposure period between three and 6 weeks frames were removed and moss analysed in the laboratory. Deposition is estimated by calculating differences in concentrations before and after exposure. Active monitoring in harsh environments (e.g. road tunnels) leads sometimes to a moss die off. This has no impact on monitoring results as the uptake of particles is independent from the physiological status of the moss (see above).

By "*passive monitoring*" moss was sampled in the field at natural growing sites of the moss. The only requirement for sampling was mostly a sufficient amount of a predetermined species in the investigation area (e.g. Zechmeister et al. 2006b). After drying at max. 40 °C moss mostly was taken into analysis without any treatment like washing. Deposition of PGE can be evaluated by analysing concentration in moss. By using adequate moss species deposition also can be allocated to a certain deposition period in the sample area.

Passive monitoring has the advantage that continuous long time monitoring, mostly up to three or more years, can be managed. This assures that concentrations are often higher than after a few weeks exposure in active monitoring and therefore results of chemical analysis are much more reliable. Up to date most of the studies presented deal with passive monitoring. On the other hand active monitoring allows for monitoring at sites without any plants growing which is often the case in polluted sites as e.g. in traffic road environments.

2 Analytical Methods

Quantification of platinum group elements requires sensitive and accurate analytical techniques like inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectrometry (ICP-AES), atomic absorption spectrometry (AAS), X-ray fluorescence (XRF), X-ray spectrometry, neutron activation analysis (NAA), adsorptive voltammetry, differential pulse polarography or proton induced X-ray emission (PIXE) (Barefoot and Van Loon, 1999; Bencs et al. 2003; Balcerzak 2011)

Over the last years, ICP-MS developed to the key routine technique in this field of application characterized by excellent sensitivity. Limit of detection (LOD) of 10 ng $L^{-1}$and 2 ng L^{-1}were reported for platinum by applying ICP-quadrupole-MS (ICP-QMS) for analysis of road side soil and dust (Whiteley and Murray 2003) and urine (Krachler et al. 1998), respectively. The introduction of sector field mass spectrometry (ICP-SFMS) further improved ion transmission efficiency compared to quadrupole based techniques resulting in significantly higher sensitivity and signal to noise ratios as can be observed in Table 1. These reported instrumental limits of detection (LOD) for platinum were expressed as three times the standard deviation of the quantified blank signal obtained by introduction of acidified ultra pure water.

In addition to improved limits of detection, the higher counting rates typical for ICP-SFMS are beneficial for measurement of accurate isotope ratios necessary for isotope dilution analysis, where counting statistics plays a major role. Separation of spectral interferences exploiting the high mass resolution power of the ICP-SFMS instrument is generally regarded as the other key advantage of ICP-SFMS. In the context of PGE analysis the application of high mass resolution settings >300 is successful in the case of a significant fraction of possible interferences. Using this instrumental setting, doubly charged ions (e.g. ^{206}Pb ++ on ^{103}Rh) and argide interferences can be separated. For Pt even oxide type interferences can be eliminated. However, several remaining prominent spectral interferences afford resolutions >12,000 for elimination. Accordingly, direct ICP-MS analysis of Pd and Rh without matrix separation becomes extremely challenging.Sample matrix and concentration ratios of the analytes of interest versus possible concomitant interfering ions in the sample have to be critically assessed (Köllensperger et al. 2000). This known problem is addressed in several reviews (Perry et al. 1995; Bencs et al.

Table 1 Recently reported limits of detection for the determination of Pt via ICP-MS

LOD of Pt	Unit	Instrument	Comment	Reference
0.008	pg g^{-1}	ICP-SFMS (Element 1, Finnigan MAT, Bremen, Germany)	MCN 100, Cetac Technologies, Omaha, NE, USA	Barbante et al. (1999)
0.007	pg g^{-1}	ICP-SFMS (Element 2, Thermo-Electron, Bremen, Germany)	MCN50, Cetac Technologies, Omaha, NE, USA	Rodushkin et al. (2004)
0.02	ng L^{-1}	ICP-SFMS (Element 1, Finnigan MAT, Bremen, Germany)	Ultrasonic, U-5000 AT^{+} (CETAC Technologies, Omaha, NB, USA)	Krachler et al. (1998)
2	ng L^{-1}	ICP-QMS (ELAN 5000, Perkin-Elmer, Norwalk, CT, USA)	Ultrasonic, U-5000 AT^{+} (CETAC Technologies, Omaha, NB, USA)	Krachler et al. (1998)
60–80	pg g^{-1}	DRC-ICP-QMS (ELAN 6100, PerkinElmer, Beaconsfield, UK)	Meinhard type nebulizer, quartz concentric spray chamber	Kan and Tanner (2004)
0.01	ng L^{-1}	ICP-QMS (Agilent 7500)	Cooled spray chamber	Whiteley and Murray (2003)

2003). The analytical approach of direct ICP-MS determination eliminating spectral interferences by membrane desolvation and additional application of high mass resolution is not valid for Pt, but not Pd, since significant interferences remain and have to be controlled. Mathematical correction procedures can only be applied after optimization for each specific sample matrix composition and concentration and is prone to errors. As a matter of fact, the ICP-MS determination of Pd in environmental samples implies the implementation of a matrix separation step, otherwise the management of a substantial number of samples in terms of quality assurance is nearly impossible. Nowadays it is well accepted that accurate analysis of Pd by IDMS in combination with matrix separationis the method of choice (Yi and Masuda 1996; Jarvis et al. 1997; Rehkämper and Halliday 1997; Müller and Heumann 2000; Hann et al. 2001; Kanitsar et al. 2003; Rudolph et al. 2006)

3 Applications—Selected Case Studies

Although the moss method could be a valuable tool for PGE monitoring up to date a comparable low number of studies on this topic have been performed. In every case Pt was analysed, in a few studies also Pd and Rh. In Table 2 concentrations found in these studies are summarized.

Table 2 Concentrations of PGE elements in bryophytes derived from various studies; concentrations are given in ng PGE/g dryweight moss; N—number of samples

Study area	Pt	Pd	Rh
Zackenberg/Northern Greenland (N = 8*)(1)	0.01 ± 5e-6	–	–
Norway (background, N = ?*)(2)	<0.1	–	–
Austria (background N = 10*)(3)	0.4 ± 0.2	–	–
Traffic sites/Austria (N = 32*)(4)	7.07 ± 9.97	2.8 ± 5.2	0.6 ± 0.8
Traffic sites/Finland (N = 35*)(5)	3.11 ± 6	–	0.9 ± 2.3
Traffic sites/France (N = ?)(6)	1.7–4.4	0.9–5.8	–
Traffic site/Germany (N = 1*)(7)	30 ± 2	2.4 ± 0.3	5.4 ± 0.5
Road Tunnel/Vienna (N = 4**)(8)	41.5 ± 9.5 (32–51)	18 ± 7 (11–25)	3.1 ± 1.4 (1.7–4.5)
Urban environment/Rome (N = 11*)(9)	3.9 ± 0.6	3.6 ± 0.2	5.3 ± 0.4
Regional/incl. Oslo (N = 40*)(10)	0.2–3.4	3.4(a)	–
Nationwide/European Arctic incl. Kola Peninsula (N = 598*)(11)	<0.2 (0.2–13.8)	0.71 (< 0.05–70.7)	–

*passive monitoring—average deposition 3 yrs

**active monitoring for 28 days; data sources are given in brackets in colume one

(a) Data from a single site, (1) Zechmeister et al. (2010), (2) Steinnes et al. (2007), (3) Zechmeister et al. unpubl.; (4) Zechmeister et al. (2006a), (5) Niemelä et al. (2007), (6) Ayrault et al. (2006), (7) Djingova et al. (2003), (8) Zechmeister et al. (2006b),(9) Beccaloni et al. (2005), (10) Reimann et al. (2006), (11) Niskavaara et al. (2004)

3.1 *Remote Areas*

As PGE pollution is a worldwide problem (see elsewhere in this book), PGE deposition can be found even in very remote areas (Moldovan, 2007). In a case study for the evaluation of background values of a series of metals and metalloids Zechmeister et al. (2010) found in the Zackenberg area (Northern Greenland) rather low concentrations in the range of 0.01 ± 5e-6 ngPt/g dryweight moss. Slightly higher background values were found by Steinnes et al. (2007) in Norway and by Zechmeister et al. (2009) in pristine Alpine areas in Austria (see Table 2).

3.2 *Traffic Sites*

Obviously most of the studies using moss as PGE monitors were related to road traffic emissions. Djingova et al. (2003) ascertained that moss showed by far higher concentrations than vascular plant species (grasses and flowering plants) which is due to different uptake mechanism and no interference of concentrations in moss with soil binding capacities.

Zechmeister et al. (2006b) conducted one of the most comprehensive study in the field of PGE monitoring deriving from road traffic emissions by analysing

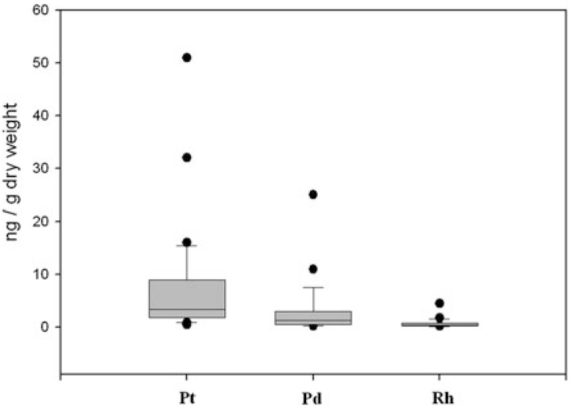

Fig. 1 Box and whisker plots of the PGE concentrations in mosses at road traffic sites in Austria (derived from Zechmeister et al. 2006b)

concentrations in mosses at a wide range of different road environments including a transect approach and road tunnel experiments (see Table 2 and Fig. 1). They showed that spatial dispersion of road related PGE deposition is largely limited to a distance of 10–200 m from the roadside however a small proportion is allocated to long range dispersal. They calculated ratios between Pt, Pd and Rh which were for Pt/Pd 7.9 ± 10.2, Pt/Rh 12.6 ± 8.3 and Pd/Rh 3.7 ± 2.2. These numbers give information on the emitting source (see elsewhere in this book). Strong correlations with Sb, Cu, Zn and Cd underlined the common origin (light duty vehicles) of these metals with those of PGE elements.

Niemelä et al. (2007) present a very similar study from Finish road sites with results comparable to those of Zechmeister et al. (2006b).

Several highways in France were explored by Ayrault et al. (2006), Concentrations ranged between 1.7 and 4.4 ngPt /g dryweight at a distance of 10 m. Pd was only detectable within a 5 m range of the roadside, which is slightly in contrast to Zechmeister et al. (2006b) who detected Pd even up to 60 m. The discrepancy might be founded in diverging analytical processes.

3.3 *Urban and Industrial Environments*

Urban environments in general provided another type of monitoring sites for studies using moss as PGE monitors. Beccaloni et al. (2005) surveyed various sites in Rome, comparing top soils with concentrations in moss. There was no clear correlation between these two matrices which could be expected taking into account the uptake process in moss. They also used different moss species at the various sites which might have influenced the results. Reimann et al. (2006) investigated a 120 km long transect in Norway passing through the capital Oslo. The strongest increases in element concentrations were found for Pt (and Au) in the Oslo area. Pd was only above detection limit at a single urban site. Probably the largest survey using mosses as biomonitors for Pt and Pd was performed by Niskavaara et al. (2004). They analysed 598 moss samples from an area of 188.000 km^2 in the European Arctic, including parts of the Kola Peninsula. Especially the Pd data set is impressive and shows spatial patterns from true background values to highly polluted sites influenced by the Russian nickel industry located on the Kola Peninsula. They compared their moss data set to various levels of soil horizons pointing at the comparable high values of Pd in moss. The Pt data set is constrained by analytical problems.

3.4 Miscellaneous

Another attempt using mosses as biomonitors or at least as biological agent for biosorption and removal of Pd(II)from aquatic solutions is described by Sari et al. (2009). They tested a range of absorption processes and described the Langmuir isotherm model as best fitting model for the uptake process. Based on their results, it can be also concluded that the *R. lanuginosum* is an effective and alternative biomass for removing Pd(II) from aqueous solution because of its high biosorption capacity, being natural and low-cost biomass.

This study is not purely included in biomonitoring studies, however gives a nice overview on sorption and retention capacities of moss in relation to PGE pollution.

4 Future Prospects

In all the presented studies it is concluded that moss is a valuable, cost efficient monitoring tool for PGE deposition studies, both in terms of spatial as well as temporal deposition patterns. Most studies highlight facts like independency of results from soil concentrations which enables the detection of true deposition deriving from objects which are wanted to be monitored (e.g. traffic, industrial complexes). In almost each study presented above Pt was analysed. Available data sets show a wide range of concentrations from true background values in the range of 0.0001 ngPt/g dry weight moss up to more than 50 ngPt/g dry weight in traffic related studies. Pd data sets are more sparsely, the same goes for Rh. In most of the surveys moss species *Pleurozium schreberi* or *Hylocomium splendens* were used which show comparable uptake efficiencies. For studies using different moss species comparison of results is sometimes hampered due to unknown uptake capacities for these species. To overcome these problems it is advised to limit to a single species preferably to those mentioned before in future monitoring studies.

Nowadays, accurate determination of PGE at ultratrace concentration levels remains a challenging task. Especially in the case of Pd, ICP-MS measurements are compromised by several interferences. Moreover, the contribution of the interference to the total signal is often significantly higher than the signal stemming from the PGE, resulting in unacceptable increase of measurement uncertainty. Analytical procedure such as matrix separation and enrichment are tedious, however cannot be avoided when aiming at accurate quantification of Pd. Moss matrix does not differ from other environmental matrices regarding PGE analytics and there are no moss specific interferences. In order to make these labor intensive methods robust and applicable to a large number of samples (high throughput), automation or on-line matrix separation procedures is addressed in ongoing analytical studies.

References

Ayrault S, Li C, Gaudry A (2006) Biomonitoring of Pt and Pd with mosses. In: Zereini F, Alt F (eds) Palladium emissions in the environment. Springer, Heidelberg p, pp 525–536

Balcerzak M (2011) Methods for the determination of platinum group elements in environmental and biological materials: a review. Crit Rev Anal Chem 41(3):214–235

Barbante C, Cozzi G, Capodaglio G, Van Velde KD, Ferrari C, Veysseyre A, Boutron CF et al (1999) Determination of Rh, Pd, and Pt in polar and alpine snow and ice by double-focusing ICPMS with microconcentric nebulization. Anal Chem 71(19):4125–4133

Barefoot RR, Van Loon JC (1999) Recent advances in the determination of the platinum group elements and gold. Talanta 49(1):1–14

Bates JW (1992) Mineral nutrition acquisition and retention by bryophytes. J Bryol 17:223–240

Bates JW, Farmer A (1992) Bryophytes and lichens in a changing environment. Clarendon Press, Oxford

Beccaloni E, Coccia AM, Musmeci L, Stacul E, Ziemacki G (2005) Chemical and microbial characterization of indigenous topsoil and mosses in green urban areas of Rome. Microchem J 79:271–289

Bencs L, Ravindra K, Van Grieken R (2003) Methods for the determination of platinum group elements originating from the abrasion of automotive catalytic converters. Spectrochim Acta Part B At Spectrosc 58(10):1723–1755

Brown DH, Bates JW (1990) Bryophytes and nutrient cycling. Bot J Linn Soc 104:129–147

Cyprien M, Barbaste M, Masson P (2008) Comparison of open digestion methods and selection of internal standards for the determination of Rh, Pd and Pt in plant samples by ICP-MS. Intern J Environ Anal Chem 88:525–537

Djingova R, Kovacheva P, Wagner G, Markert B (2003) Distribution of platinum group elements and other traffic related elements among different plants along some highways in Germany. Sci Total Environ 308:235–246

Gjengedahl E, Steinnes E (1990) Uptake of metal ions in moss from artificial precipitation. Environ Monit Assess 14:77–87

Glime JM (2009) Bryophyte ecology. Physiological Ecology, vol 1. Ebook sponsored by Michigan Technological University and the International Association of Bryologists. http://www.bryoecol.mtu.edu/. Accessed 28 Aug 2013

Hann S, Koellensperger G, Kanitsar K, Stingeder G (2001) ICP-SFMS determination of palladium using IDMS in combination with on-line and off-line matrix separation. J Anal At Spectrom 16 (9):1057–1063

Harmens H, Ilyin I, Mills G, Aboal JR, Alber R, Blum O, Carballeira A, Coşkun M, De Temmerman L, Fernnandez JA, Figuera R, Frontasevya M, Godzik B, Goltsova N, Jeran Z, Korzewka S, Kubin E, Kvietkus K, Leblond S, Liiv S, Magnusson SH, Maňkovská B, Nikodemus O, Pesch R, Poikolainen J, Radnovic D, Rühling A, Santamaría J, Schröder W, Spiric Z, Stafilov T, Steinnes E, Suchara I, Tabors G, Thöni L, Turcsanyi G, Yurukova L, Zechmeister HG (2012) Country-specific correlations across Europe between modelled atmospheric cadmium and lead depositon and concentrations in mosses. Environ Pollut 166:1–9

Jarvis I, Totland MM, Jarvis KE (1997) Assessment of dowex 1-X8 based anion-exchange procedures for the separation and determination of ruthenium, rhodium, palladium, iridium, platinum and gold in geological samples by inductively coupled plasma mass spectrometry. Analyst 122(1):19–26

Kan SF, Tanner PA (2004) Determination of platinum in roadside dust samples by dynamic reaction cell-inductively coupled plasma-mass spectrometry. J Anal At Spectrom 19 (5):639–643

Kanitsar K, Koellensperger G, Hann S, Limbeck A, Puxbaum H, Stingeder G (2003) Determination of Pt, Pd and Rh by inductively coupled plasma sector field mass spectrometry (ICP-SFMS) in size-classified urban aerosol samples. J Anal At Spectrom 18(3):239–246

Köllensperger G, Hann S, Stingeder G (2000) Determination of Rh, Pd and Pt in environmental silica containing matrices: Capabilities and limitations of ICP-SFMS. J Anal At Spectrom 15 (12):1553–1557

Krachler M, Alimonti A, Petrucci F, Irgolic KJ, Forastiere F, Caroli S (1998) Analytical problems in the determination of platinum-group metals in urine by quadrupole and magnetic sector field inductively coupled plasma mass spectrometry. Anal Chim Acta 363(1):1–10

Markert BA, Breure AM, Zechmeister HG (eds) (2003) Bioindicators / Biomonitors (principles, assessment, concepts). Elsevier, Amsterdam

Moldovan M (2007) Origin and fate of platinum group elements in the environment. Anal Bioanal Chem 388(3):537–540

Müller M, Heumann KG (2000) Isotope dilution inductively coupled plasma quadrupole mass spectrometry in connection with a Chromatographic separation for ultra trace determinations of platinum group elements (Pt, Pd, Ru, Ir) in environmental samples. Fresenius' J Anal Chem 368(1):109–115

Niemelä M, Piispanen J, Poikolainen J, Perämäki P (2007) Preliminary study of the use of terrestrial moss (*Pleurozium schreberi*) for biomonitoring traffic-related Pt and Rh deposition. Arch Environ Contam Toxicol 52:347–354

Niskavaara H, Kontas E, Reimann C (2004) Regional distribution and sources of Au, Pd and Pt in moss and O-, B- and C-horizon podzol samples in the European Arctic. Geochem: Explor Environ Anal 4:143–159

Pakarinen P, Rinne RJK (1979) Growth rates and heavy metal concentrations of five moss species in paludified spruce forests. Lindbergia 5:77–83

Perry BJ, Barefoot RR, Van Loon JC (1995) Inductively coupled plasma mass spectrometry for the determination of platinum group elements and gold. Trends Anal Chem 14(8):388–397

Popper ZA, Fry SC (2003) Primary cell wall composition of bryophytes and charophytes. Ann Bot 91:1–12

Rehkämper M, Halliday AN (1997) Development and application of new ion-exchange techniques for the separation of the platinum group and other siderophile elements from geological samples. Talanta 44(4):663–672

Reimann C, Arnoldussen A, Boyd R, Finne TE, Nordgulen Ø, Volden T, Englmaier P (2006) The influence of a city on element contents of a terrestrial moss (*Hylocomium splendens*). Sci Total Environ 369:419–432

Rodushkin I, Engström E, Stenberg A, Baxter DC (2004) Determination of low-abundance elements at ultra-trace levels in urine and serum by inductively coupled plasma-sector field mass spectrometry. Anal Bioanal Chem 380(2):247–257

Rudolph E, Limbeck A, Hann S (2006) Novel matrix separation - On-line pre-concentration procedure for accurate quantification of palladium in environmental samples by isotope dilution inductively coupled plasma sector field mass spectrometry. J Anal At Spectrom 21 (11):1287–1293

Rűhling Å, Tyler G (1970) Sorption and retention of heavy metals in the woodland moss *Hylocomium splendens* (Hedw.) Br. et Sch. Oikos 21:92–97

Sari A, Mendil D, Tuzen M, Soylak M (2009) Biosorption of palladium(II) from aqueous solution by moss (*Racomitrium lanuginosum*) biomass: Equilibrium, kinetic and thermodynamic studies. J Hazard Mater 162:874–879

Smith AJE (1983) Bryophyte ecology. Chapman and Hall, London

Steinnes E, Berg T, Uggerud H, Vadset M (2007) Atmosfærisk nedfall av tungmetaller I Norge. Landsomfattende undersøkelsei 2005. NTU, Norway, TA-2241/2007

Vanderpoorten A, Goffinet B (2009) Introduction to bryophytes. Cambridge University Press, Cambridge

Whiteley JD, Murray F (2003) Anthropogenic platinum group element (Pt, Pd and Rh) concentrations in road dusts and roadside soils from Perth, Western Australia. Sci Total Environ 317(1–3):121–135

Yi YV, Masuda A (1996) Simultaneous Determination of Ruthenium, Palladium, Iridium, and Platinum at Ultratrace Levels by Isotope Dilution Inductively Coupled Plasma Mass Spectrometry in Geological Samples. Anal Chem 68(8):1444–1450

Zechmeister HG (1998) Annual growth of four pleurocarpous moss species and their applicability for biomonitoring heavy metals.Environmental Monitoring. Assessment 52:441–451

Zechmeister HG, Dullinger S, Koellensperger G, Ertl S, Lettner C, Reiter K (2010) Do metal concentrations in moss from the Zackenberg area, Northeast Greenland, provide a baseline for monitoring? Environ Sci Pollut Res 18:91–98

Zechmeister HG, Dullinger S, Hohenwallner D, Riss A, Hanus-Illnar A, Scharf S (2006a) Pilot study on road traffic emissions (PAHs, heavy metals) measured by using mosses in a tunnel experiment in Vienna, Austria. Environ Sci Pollut Res 13:398–405

Zechmeister HG, Hagendorfer H, Hohenwallner D, Riss A, Hanus-Illnar A (2006b) Analysis of Platinum group elements in mosses as indicators of road traffic emissions in Austria. Atmos Environ 40:7720–7732

Zechmeister HG, Grodzinska K, Szarek-Lukaszewska G (2003) Bryophytes. In: Markert BA, Breure AM, Zechmeister HG (eds) Bioindicators / Biomonitors (principles, assessment, concepts). Elsevier, Amsterdam, pp 329–375

Zechmeister HG, Hohenwallner D, Hanus-Illnar A, Roder I, Riss A (2009) Schwermetalldepositionen in Österreich—erfasst durch Biomonitoring mit Moosen. (Aufsammlung 2005). Report des Umweltbundesamtes Wien 0201, Wien

Field Studies on PGE in Aquatic Ecosystems

Nadine Ruchter, Sonja Zimmermann and Bernd Sures

Abstract Aquatic ecosystems can be considered as an important sink of platinum group elements. Different sources, like road runoff or industrial effluents are directly discharged into aquatic ecosystems. This article summarizes the recent knowledge on PGE (mainly Pt, Pd, and Rh) in aquatic ecosystems. It analyzes different routes into freshwater and saltwater systems, and summarizes the concentrations in the relevant matrices like water, sediments and biota. Results of our literature analysis show, that PGE can be detected in all matrices analyzed originating from all aquatic ecosystems investigated. Several studies further indicate that concentrations are still rising. It is further evident, that there is still a lack of data concerning the bioavailability of all PGE for aquatic plants and animals and that there is still a need of well performed and documented field studies.

1 Introduction

Even though research on Platinum Group Elements (PGE) is performed for more than 2 decades by now, the distribution of PGE and concentration ranges in natural ecosystems remains unclear. Up to now, a clear risk assessment for PGEs cannot be done. This is due to the fact that field studies are rare. As PGE are not analyzed in standardized monitoring programs, environmental data is only available from studies specifically concentrating on PGE. Furthermore, due to the fact that the analytical methods for PGE determination in environmental concentration ranges as well as in different environmental matrices is rather sophisticated, it is not surprising that there is still a lack of environmental relevant data. Especially aquatic ecosystems are thought to be one important sink for PGE (Haus et al. 2007), as road

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runoff and industrial effluents are directly discharged into rivers. However, next to rivers also other aquatic ecosystems might be effected by PGE.

This article summarizes and discusses the up to date knowledge on concentration ranges, routes and distribution of PGE in different aquatic ecosystems. First, it focuses on freshwater systems, which can be distinguished into lentic systems, like ponds and lakes in which water often has no current, and lotic systems like rivers, in which water is running and also sediments are in a directional movement. Subsequently, the article addresses saltwater systems, like estuaries, a zone were freshwater of the river is meeting the saltwater of the sea, and oceans. Due to the fact that most often only Pt, Pd, and Rh were analyzed in aquatic ecosystems this article will clearly focus on those three PGE. However, whenever available, data on Ru, Ir, and Os are also reported.

2 Lentic Water Ecosystems: Lakes and Ponds

Freshwater lakes are a good starting point to analyzing the anthropogenic input of PGE into aquatic ecosystems. As metals accumulate in lake sediments, sediment cores can be used as pollutant archives, telling us the history of metal input into the system. With the help of geological methods, a specific layer of a sediment core can be assigned to a specific time period. Three research groups (Lee 1983; Rauch and Hemond 2003; Rauch et al. 2004) used such lake sediment cores to investigate the environmental concentration changes of all six PGE within the last century.

Lee (1983) analyzed Pd in sediment cores of a moat from the Palace in Tokyo: Sediment layers were dated to originate from 1948 to 1973. Layers from 1948 to 1963 showed a constant Pd concentration of approx. 2 ng/g, whereas the Pd concentrations in layers from 1970 to 1973 increased constantly to a maximum of 46 ng/g in 1973. A similar approach investigated retrospective concentrations of Pt, Pd, Rh, Ru, Ir and Os in sediment cores of the Upper Mystik Lake in Boston (Rauch and Hemond 2003; Rauch et al. 2004): Concentrations in sediment layers dated prior to 1975 ranged between 0.5 and 2.3 ng/g for Pt, approx. 2 ng/g for Pd and 1 ng/g for Rh. Starting in the 1980s, concentrations of Pt, Pd and Rh increased to 29, 21 and 3 ng/g, respectively. Levels of the three metals were positively correlated and ratios of Pt/Rh and Pd/Rh resembled those ratios which are found in automobile catalyst converters. In contrast, Ir and Ru concentrations were constant throughout the analyzed time periods with only a slight increase in the very recent years. Therefore, the authors concluded that Pt, Pd and Rh were introduced via road runoff, while the recent increase of Ir and Ru could be a result of impurities of the PGE in automobile catalytic converters.

If and to which degree the introduction of PGE into standing water systems has any consequences for biota is up to now not sufficiently investigated. The only study available focused on Pt concentrations in the crustaceans *Gammarus pulex*, *Gammarus fossarum* and *Asellus aquaticus* from different lakes of the Ruhr district, a heavily urbanized region in Germany, and revealed Pt concentrations above the

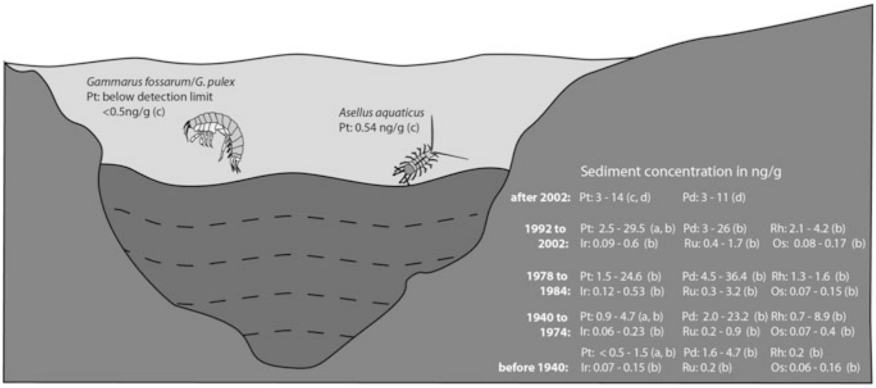

Fig. 1 Literature data of PGE concentrations in lake systems: **a** Rauch and Hemond (2003), **b** Rauch et al. (2004), **c** Haus et al. (2007), **d** Jackson et al. (2007)

detection limit in *A. aquaticus*, proving the availability of Pt for animals in lake systems (Haus et al. 2007). Concentrations of all six PGE in different matrices of lentic water systems are summarized in Fig. 1.

3 Flowing-Water Systems: Rivers and Streams

Among all aquatic ecosystems investigated most information on PGE is available for rivers for which several PGE sources were reported. In addition to direct discharges through industry and waste water treatment plants, which often combine PGE from road runoff, hospitals, dental clinics etc. (IWW 2004) diffuse discharges due to highway runoff were reported (IWW 2004). PGE concentrations were analyzed in water (Pt, Pd, Rh, Ir) and sediment samples (Pt, Pd, Rh, Ir, Ru) as well as in animals (Pt, Pd, Rh) (see Fig. 2). However, no information is available on environmental PGE concentrations in aquatic plants.

PGE concentrations in water samples most often ranged near or below the analytical detection limits (see Fig. 2). Unfortunately, in most of the studies cited in Fig. 2, the sampling points are barely described. Therefore, it is often unclear, if there is a source for PGE near the sampling point or if the samples were taken in urban or rural areas. Concentrations of Pd in river water samples varied between 0.4 and 10.7 ng/L, whereas the Pt and Rh concentrations of the same samples were described to be below the detection limit of 0.9 and 0.5 ng/L, respectively (Eller et al. 1989; Moldovan et al. 2003). In contrast, Hoppstock and Alt (2000) analyzed Pt concentrations of up to 0.8 ng/L in water samples of the river Elbe, Germany. Ir concentrations in aqueous samples analyzed by negative thermal ionization mass spectrometry (NTIMS) ranged between 17 and 92 (10^8 atoms/kg), which corresponds to 0.37–2 pg Ir/L (Anbar et al. 1996). In comparison, Odiyo et al. (2005) analyzed Pt and Pd in water samples of urban rivers. They found PGE

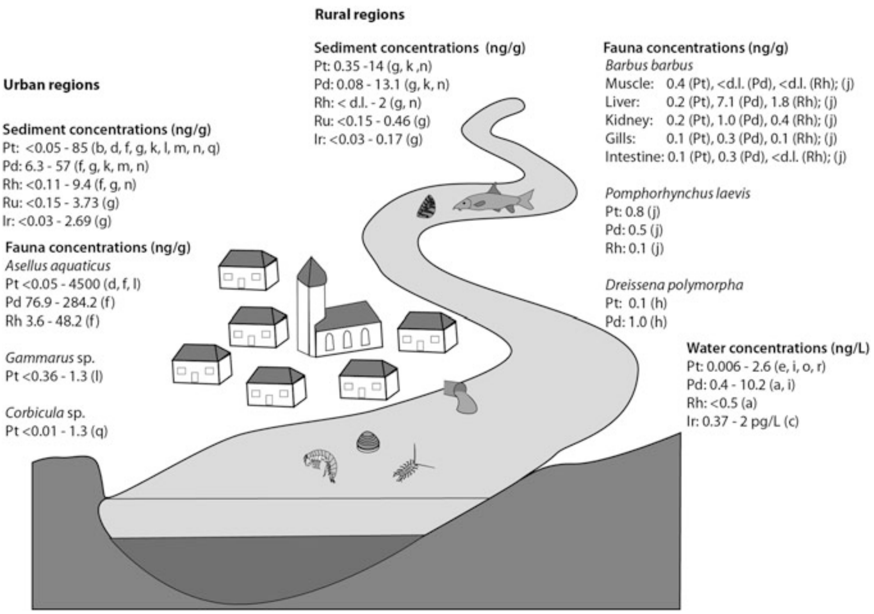

Fig. 2 Literature data of PGE concentrations in river environments. **a** Eller et al. (1989), **b** Wei and Morrison (1994), **c** Anbar et al. (1996), **d** Rauch and Morrison (1999), **e** Hoppstock and Alt (2000), **f** Moldovan et al. (2001), **g** de Vos et al. (2002), **h** Zimmermann et al. (2002), **i** Moldovan et al. (2003), **j** Sures et al. (2005), **k** Pratt and Lottermoser (2007), **l** Haus et al. (2007), **m** Jackson et al. (2007), **n** Prichard et al. (2008), **o** Monticelli et al. (2010), **p** Locatelli (2011), **q** Ruchter (2012), **r** Cobelo-García et al. (2013)

concentrations of up to 10 µg/L for Pt and 3.3 µg/L for Pd, which is three orders of magnitudes higher as compared with the former studies and the Pt concentrations even exceeded the Cu concentrations within the same study. The authors suggest that the Pt and Pd pollution may be caused by effluents of sewage systems and therefore originates from households with jewelry and from automobile catalytic converters. However, as the analyses were performed with ICP-OES, which usually has rather high detection limits for PGE and shows many interferences, analytical problems cannot be excluded. Unfortunately, quality assurance data for the PGE analyses were not given in this study.

Excluding the study of Odiyo et al. (2005), it can be summarized that highest aqueous PGE concentrations were reported for Pd (13.1 ng/L, Moldovan et al. 2001) followed by Pt (2.6 ng/L, Monticelli et al. 2010) and Ir (0.002 ng/L, Anbar et al. 1996), whereas Rh levels were below the detection limit (Eller et al. 1989). To the knowledge of the authors, no data is available for Ru or Os.

PGE concentrations were analyzed in river sediments of different countries such as Australia (Pratt and Lottermoser 2007), UK (de Vos et al. 2002; Jackson et al. 2007; Prichard et al. 2008), Germany (Haus et al. 2007; Ruchter 2012), and Sweden (Wei and Morrison 1994; Rauch and Morrison 1999; Moldovan et al. 2003).

Table 1 Ratios of PGE in sediment samples

Pt/Pd ratio	Pt/Rh ratio	Pd/Rh ratio	Reference
0.5–2.8	2–17.5	2–12.5	Prichard et al. (2008)
1.38	–	–	Jackson et al. (2007)
1.9	–	–	Pratt and Lottermoser (2007)
0.6–4.3	6.2–18.4	2–24	De Vos et al. (2002)
1.2–1.6	6	3.7–4.5	Moldovan et al. (2001)

Unfortunately, due to the use of different preparation methods different grain size classes were analyzed which makes a comparison of data from different studies difficult. Despite these inconsistencies, concentrations of Pt, Pd, Rh, Ru, and Ir in river sediments varied in the low ng/g range (see Fig. 2), whereas for Os no published data could be found. Furthermore, it appears that concentrations of the analyzed PGE in sediments of urban rivers exceed the respective rural levels (see Fig. 2). Accordingly, Haus et al. (2010) suggested, that sediments containing 20 ng/g Pt and/or Pd can be assumed to be highly polluted, while low polluted sediments reveal Pt and/or Pd concentrations below 10 ng/g. In order to analyze the sources of PGE in sediments, PGE ratios were often used. Rauch et al. (2004) for example, found PGE ratios in lake sediment samples which were in accordance to PGE ratios used in automobile catalytic converters. In river sediments however, the ratios found for Pt/Pd, Pt/Rh and Pd/Rh vary highly, both between different studies and within the same study. General conclusions regarding the mobility of the different PGE are therefore difficult to draw. This becomes obvious when considering the studies of de Vos et al. (2002) and Prichard et al. (2008). Here, a high number of different sampling sites were monitored and Pt/Pd ratios were found below and above 1. Even though it is stated, that Pd is substituting Pt in automobile catalytic converters, Table 1 does not show any time-based trend of the Pt/Pd ratio. Therefore, the high variability between the PGE ratios is rather explained by different PGE sources than by Pd/Pt substitution.

While most of the studies published so far solely focus on the analysis of PGE, a few studies (Haus et al. 2007; Pratt and Lottermoser 2007; Ruchter 2012) compared concentrations of PGE and other heavy metals in sediments. These found PGE concentrations in sediments to be 2–3 orders of magnitude lower than those of other heavy metals. For example, Pt concentrations of urban river sediments ranged in a low ng/g range, whereas in the same samples concentrations of Ag and Cd varied in a high ng/g to a low µg/g range and concentrations of Ni, Cr, Cu, Pb, and Zn were found in a µg/g range (Ruchter 2012).

With respect to PGE concentrations in animals different taxa were analyzed comprising fish (*Barbus barbus*, Sures et al. 2005), crustaceans (*Asellus aquaticus*, *Gammarus fossarum*, *Gammarus pulex*, Rauch and Morrison 1999; Moldovan et al. 2001; Haus et al. 2007) and molluscs (*Dreissena polymorpha*, *Corbicula* sp. in Zimmermann et al. 2002; Ruchter 2012). Barbels as well as zebra mussels were collected in rural areas and were analyzed for their PGE concentrations prior to their use as test organisms in laboratory studies. In freeze dried soft tissue of zebra mussels from Lake Mondsee, Austria, mean PGE concentrations of 0.1 ng/g Pt and 1 ng/g Pd were found (Zimmermann et al. 2002). Barbels from the river Danube about 30 km downstream of the city of Budapest, Hungary were analyzed for Pt, Pd and Rh in different tissues (muscle, liver, intestine), revealing that concentrations were highest in the liver with 7.1 ng/g for Pd and 1.8 ng/g for Rh. Pt levels were highest in parasites (*Pomphorhynchus laevis*) of barbel with 0.8 ng/g followed by muscle tissue with 0.4 ng/g (Sures et al. 2005). This is in accordance with results of laboratory exposure studies as described in book Chap. "Laboratory Studies on the Uptake and Bioaccumulation of PGE by Aquatic Plants and Animals" of Zimmermann et al.

In addition to animal samples from rural sites animals of urban river segments were investigated, with *Asellus aquaticus* being the most frequently investigated species. Pt, Pd and Rh concentrations in *A. aquaticus* sampled at different sites in Sweden and Germany were found to be highly variable (from below detection limit to 4,500 ng/g) (Rauch and Morrison 1999; Moldovan et al. 2001; Haus et al. 2007). The high variance could be explained by different sampling sites and times, and by the use of different analytical procedures. Additionally, Rauch and Morrison (1999) found that Pt concentrations in asselids are dependent on the moulting status of the animals. As the animals store approximately 75 % of the accumulated Pt in their exoskeleton, asselids can lose a huge amount of Pt just by moulting. Further factors, which influence PGE accumulation in aquatic organisms are explained by Zimmermann et al., in Chap. "Laboratory Studies on the Uptake and Bioaccumulation of PGE by Aquatic Plants and Animals" of this book.

Concentrations of Pt were also analyzed for gammarids and the Asian clam (*Corbicula* sp.). For both taxa maximum Pt concentration were found to be 1.3 ng/g. The animals were caught at urban sampling sites with high Pt concentrations in the sediment samples (Haus et al. 2007; Ruchter 2012). Although all studies conducted so far clearly indicate that Pt, Pd, and Rh are introduced into natural river systems and that they are available for animals under field conditions none revealed a correlation between sediment and biota concentrations.

4 Platinum Group Elements in Estuaries and Marine Ecosystems

Some of the earliest experiments for the establishment of analytical procedures to determine PGE in environmental samples were conducted with sea water (Lee 1983; Hodge et al. 1986), followed by a number of studies from other authors. Literature data on PGE concentrations in water of estuaries and oceans unravel clear gradients (summarized in Fig. 3). Pt levels in water samples of the open ocean are far below water concentrations near the coast, e.g. in estuaries and at the continental shelf. This can be interpreted as an indication of anthropogenic Pt input from rivers into the marine environment which is associated with a change in ion speciation (Cobelo-García et al. 2013). Cobelo-García et al. (2013) concluded from results of laboratory experiments with different water types that salt water reduced the

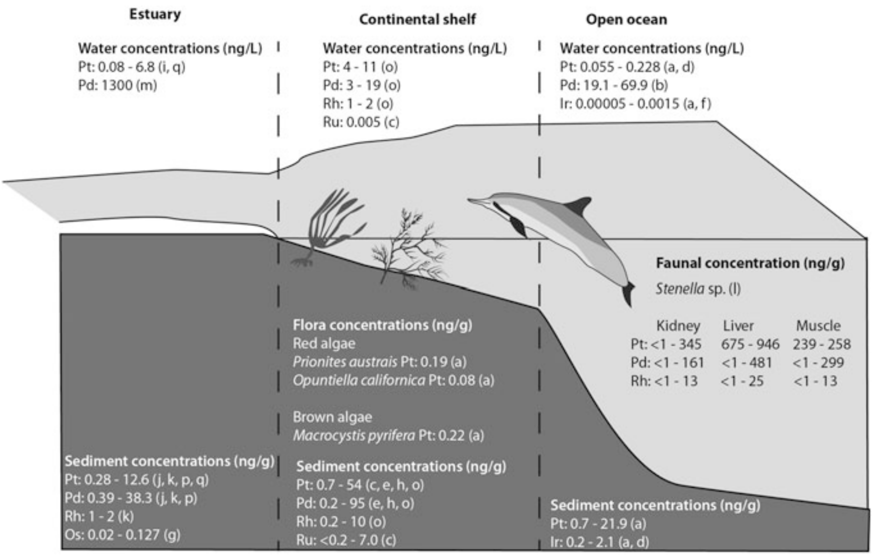

Fig. 3 PGE concentrations in estuaries and oceans. **a** Hodge et al. (1986), **b** Lee (1983), **c** Koide et al. (1986), **d** Colodner et al. (1993), **e** Terashima et al. (1993), **f** Anbar et al. (1996), **g** Williams et al. (1997), **h** Tuit et al. (2000), **i** Obata et al. (2006), **j** Pratt and Lottermoser (2007), **k** Prichard et al. (2008), **l** Essumang (2008), **m** Bonanno (2011), **n** Cobelo-García et al. (2011), **o** Essumang and Adokoh (2011), **p** Zhong et al. (2012), **q** Cobelo-García et al. (2013)

reactivity of Pt particles and increased the proportion of dissolved Pt as compared with fresh water. This Pt concentration decrease from coastal to open ocean areas samples cannot be observed for other PGE, as the data basis for the other PGE is too low. Extraordinary high aqueous Pd concentrations in estuarine water samples of up to 1.3 µg/L were described by Bonanno (2011), whereas Pd concentrations in water samples of rivers (see Fig. 2), continental shelves, and open oceans (see Fig. 3) were reported to be in a low ng/L range. However, Bonanno (2011) used ICP-MS analysis for the Pd determination without appropriate validation of their analytical procedure although it is known that this detection method without matrix separation and/or mathematical correction bears problems due to mass interferences (Bencs et al. 2003; Balcerzak 2011).

The second concentration gradient is an increase of aqueous Pt and Pd concentrations with water depth in open oceans (Hodge et al. 1985, 1986; Lee 1983, van den Berg and Jacinto 1988). Hodge et al. (1986) called this distribution the “nutrient like profile”, which was previously also described for Ni.

In marine sediments, PGE concentrations were found in a wide concentration range (Fig. 3). For estuary and continental shelf samples, the concentration range in sediment samples resemble that of river systems. Similar to lake sediments depth profiles of Pt concentrations were taken for estuary sediments (Cobelo-García et al. 2011) showing higher Pt concentration at the sediment surface compared to deeper areas indicating a relatively recent Pt discharge into estuarine systems.

With respect to biota only limited information is available for marine environments as they derive from only three studies (Hodge et al. 1986; Essumang 2008; Essumang et al. 2008). Pt concentrations were analyzed in three different algae species (Hodge et al. 1986), whereas Essumang and coworkers reported on concentrations of Pt, Pd and Rh in various marine animal species (Essumang et al. 2008; Essumang 2008). In the latter study the Pt, Pd and Rh concentrations in the different tissues of four individual dolphins decreased in the following order: liver > muscle > kidney and were highest for Pt, followed by Pd and Rh. Furthermore, Essumang et al. (2008) analyzed PGE in fish, crabs, prawns and a mollusk species. However, due to discrepancies in the described preparation methods (taxa remain unclear; although different tissues were analyzed whole species PGE levels were presented) the values are not referred to in this chapter.

5 Conclusions

In summary, it could be shown that PGE can be found in all types of aquatic ecosystems such as lakes, rivers, estuaries and oceans although there is still a lack of environmental PGE data. Concentrations of PGE are higher in urban areas compared to rural areas and near the coast compared to open oceans. This clearly suggests an anthropogenic influence of PGE distribution in the environment starting with the introduction of automobile catalytic converters. Nowadays, however, it appears that multiple sources for the introduction of PGE into aquatic systems exist. Due to sediment core analyses it can further be stated that concentrations are rising. The most often analyzed PGE are Pt, Pd and Rh, while information for Ir, Ru and Os is scarce. Pt, Pd and Rh accumulate in sediments and are available for organisms. In all matrices analyzed so far PGE concentrations are relatively low compared to other heavy metals. From the selected number of studies describing unusually high PGE levels it can be concluded, that PGE analysis in ultra-trace concentration ranges is still a challenge and data should be accompanied by a thorough description of analytical validation. Furthermore, reference material for PGE analysis at low environmental concentrations is still scarce and not available for biological materials, which makes analytical validation challenging. Finally, PGE are not part of governmental monitoring systems, which might be one reason for the paucity of data on their distribution in aquatic environmental matrices, especially in plants and animals. Accordingly, monitoring programs on PGE should be conducted in the future.

References

Anbar A, Wasserburg G, Papnastassiou D, Andersson PS (1996) Iridium in natural waters. Science 273:1524–1528

Balcerzak M (2011) Methods for the determination of platinum group elements in environmental and biological materials: A review. Crit Rev Environ Sci Technol 41:214–235

Bencs L, Ravindra K, Van Grieken R (2003) Methods for the determination of platinum group elements originating from the abrasion of automotive catalytic converters. Spectrochim Acta Part B 58:1723–1755

Bonanno G (2011) Trace element accumulation and distribution in the organs of *Phragmites australis* (common reed) and biomonitoring applications. Ecotoxicol Environ Saf 74:1057–1064

Cobelo-García A, López-Sánchez DE, Almécija C, Santos-Echeandía J (2013) Behavior of platinum during estuarine mixing (Pontevedra Ria, NW Iberian Peninsula). Mar Chem 150:11–18

Cobelo-García A, Neira P, Mil-Homens M, Caetano M (2011) Evaluation of the contamination of platinum in estuarine and coastal sediments (Tagus Estuary and Prodelta, Portugal). Mar Pollut Bull 62:646–650

Colodner DC, Boyle EA, Edmond JM (1993) Determination of rhenium and platinum in natural waters and sediments, and iridium in sediments by flow injection isotope dilution inductively coupled plasma mass spectrometry. Anal Chem 65:1419–1425

De Vos E, Edwards S, McDonald I, Wray D, Carey P (2002) A baseline survey of the distribution and origin of platinum group elements in contemporary fluvial sediments of the Kentish Stour. England Appl Geochem 17:1115–1121

Eller R, Alt F, Tölg G, Tobschall HJ (1989) An efficient combined procedure for the extreme trace analysis of gold, platinum, palladium and rhodium with the aid of graphite furnace atomic absorption spectrometry and total-reflection X-ray fluorescence analysis. Fresenius Z Anal Chem 334:723–739

Essumang D (2008) Bioaccumulation of platinum group metals in dolphins, *Stenella* sp., caught off Ghana. Afr J Aquat Sci 33:255–259

Essumang D, Adokoh C (2011) Deposition of platinum-group metals in sediment and water bodies along the coastal belt of Ghana. Maejo Int J Sci Technol 5:331–349

Essumang DK, Dodoo DK, Adokoh CK, Sam A, Doe NG (2008) Bioaccumulation of platinum group metals on some fish species (*Oreochromis niloticus*, *Penaeus laspisulcates*, *Scylla serrate*, *Galaxias brevipinnis* and Mollusc) in the Pra estuary of Ghana. Toxicol Environ Chem 90:625–638

Haus N, Zimmermann S, Sures B (2010) Precious metals in urban aquatic systems: platinum, palladium and rhodium: sources, occurrence, bioavailability and effects. In: Fatta-Kasinos D, Bester K, Kümmerer K (eds) Xenobiotics in the urban water cycle mass flows, processes, mitigation and treatment strategies. Springer, The Netherlands, pp 73–86

Haus N, Zimmermann S, Wiegand J, Sures B (2007) Occurrence of platinum and additional traffic related heavy metals in sediments and biota. Chemosphere 66:619–629

Hodge V, Stallard M, Koide M, Goldberg ED (1986) Determination of platinum and iridium in marine waters, sediments, and organisms. Anal Chem 58:616–620

Hodge VF, Stallard M, Koide M, Goldberg ED (1985) Platinum and the platinum anomaly in the marine environment. Earth Planet Sci Lett 72:158–162

Hoppstock K, Alt F (2000) Voltammetric determination of ultratrace platinum and rhodium in biological and environmental samples. In: Zereini F, Alt F (eds) Anthropogenic platinum-group element emissions. Springer, New York, pp 146–154

IWW (2004) Untersuchungen zum Eintrag von Platingruppenelementen verschiedener Emittenten in Oberflächengewässer des Landes Nordrhein-Westfalen. Rheinisch-Westfälisches Institut Wasserforschung. Im Auftrag des Ministeriums für Umwelt und Naturschutz, Landwirtschaft und Verbraucherschutz des Landes Nordrhein-Westfalen; Aktenzeichen IV-9-042 529 Abschlussbericht

Jackson MT, Sampson J, Prichard HM (2007) Platinum and palladium variations through the urban environment: evidence from 11 sample types from Sheffield. UK Sci Total Environ 385:117–131

Koide M, Stallard M, Hodge V, Goldberg ED (1986) Preliminary studies on the marine chemistry of ruthenium. Netherlands J Sea Res 20:163–166

Lee DS (1983) Palladium and nickel in north-east Pacific waters. Nature 305:47–48

Locatelli C (2011) Catalytic-adsorptive stripping voltammetric determination of ultra-trace iridium (III). Application to fresh- and sea-water. Talanta 85:546–550

Moldovan M, Gomez MM, Palacios MA, Gómez M (2003) On-line preconcentration of palladium on alumina microcolumns and determination in urban waters by inductively coupled plasma mass spectrometry. Anal Chim Acta 478:209–217

Moldovan M, Rauch S, Gomez M, Palacios MA, Morrison GM (2001) Bioaccumulation of palladium, platinum and rhodium from urban particulates and sediments by the freshwater isopod *Asellus aquaticus*. Water Res 35:4175–4183

Monticelli D, Carugati G, Castelletti A, Recchia S, Dossi C (2010) Design and development of a low cost, high performance UV digester prototype: application to the determination of trace elements by stripping voltammetry. Microchem J 95:158–163

Obata H, Yoshida T, Ogawa H (2006) Determination of picomolar levels of platinum in estuarine waters: a comparison of cathodic stripping voltammetry and isotope dilution-inductively coupled plasma mass spectrometry. Anal Chim Acta 580:32–38

Odiyo JO, Bapela HM, Mugwedi R, Chimuka L (2005) Metals in environmental media: A study of trace and platinum group metals in Thohoyandou, South Africa. Water SA 31:581–588

Pratt C, Lottermoser BG (2007) Mobilisation of traffic-derived trace metals from road corridors into coastal stream and estuarine sediments, Cairns, northern Australia. Environ Geol 52:437–448

Prichard H, Jackson M, Sampson J (2008) Dispersal and accumulation of Pt, Pd and Rh derived from a roundabout in Sheffield (UK): from stream to tidal estuary. Sci Total Environ 401:90–99

Rauch S, Hemond HF (2003) Sediment-based evidence of platinum concentration changes in an urban lake near Boston, Massachusetts. Environ Sci Technol 37:3283–3288

Rauch S, Hemond HF, Peucker-Ehrenbrink B, Section E (2004) Recent changes in platinum group element concentrations and osmium isotopic composition in sediments from an urban lake. Environ Sci Technol 38:396–402

Rauch S, Morrison GMM (1999) Platinum uptake by the freshwater isopod *Asellus aquaticus* in urban rivers. Sci Total Environ 235:261–268

Ruchter N (2012) Ecotoxicology of traffic related platinum in the freshwater environment. Phd thesis, University of Duisburg-Essen

Sures B, Thielen F, Baska F, Messerschmidt J, Bohlen VA (2005) The intestinal parasite *Pomphorhynchus laevis* as a sensitive accumulation indicator for the platinum group metals Pt, Pd, and Rh. Environ Res 98:83–88

Terashima S, Katayama H, Itoh S (1993) Geochemical behavior of Pt and Pd in coastal marine sediments, southeastern margin of the Japan Sea. Appl Geochem 8:265–271

Tuit CB, Ravizza GE, Bothner MH (2000) Anthropogenic platinum and palladium in the sediments of Boston harbor. Environ Sci Technol 34:927–932

Van den Berg CMG, Jacinto GS (1988) The determination of platinum in sea water by adsorptive cathodic stripping voltammetry. Anal Chim Acta 211:129–139

Wei C, Morrison GM (1994) Platinum in road dusts and urban river sediments. Sci Total Environ 147:169–174

Williams G, Marcantonio F, Turekian KK (1997) The behavior of natural and anthropogenic osmium in Long Island Sound, an urban estuary in the eastern U.S. Earth Planet Sci Lett 148:341–347

Zhong L-F, Yan W, L, J, Tu X-L, Liu B-M, Xia Z (2012) Pt and Pd in sediments from the Pearl River Estuary, South China: background levels, distribution, and source. Environ Sci Pollut Res Int 19:1305–1314

Zimmermann S, Alt F, Messerschmidt J, von Bohlen A, Taraschewski H, Sures B (2002) Biological availability of traffic-related platinum-group elements (palladium, platinum, and rhodium) and other metals to the zebra mussel (*Dreissena polymorpha*) in water containing road dust. Environ Toxicol Chem 21:2713–2718

Laboratory Studies on the Uptake and Bioaccumulation of PGE by Aquatic Plants and Animals

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Abstract The present book chapter gives an overview of laboratory exposure experiments dealing with the biological availability, uptake and accumulation of the platinum group elements (PGE) platinum, palladium and rhodium by aquatic organisms. Effects of different test parameters such as test system, PGE source, route of exposure, exposure concentration, exposure medium, test organism, temperature and exposure period are described in detail. Problems in the determination of bioaccumulation factors (BAF) and in their use to comparing results from different bioaccumulation studies are discussed. Although the transfer of laboratory results to field conditions bears a lot of difficulties, it is important to know these influences and problems for a better understanding of the environmental situation.

1 Introduction

The key sources for environmental contamination with the platinum group elements (PGE) platinum, palladium and rhodium are automobile catalytic converters, hospitals, dental laboratories and PGE-using industries (summarized in Hoppstock and Sures 2004). Field studies show, that these noble metals are introduced into aquatic habitats where they accumulate in the sediments (summarized in Zereini and Alt 2000; Hoppstock and Sures 2004; Haus et al. 2010) and get in contact with biota (Haus et al. 2007). The present book chapter updates the state of knowledge (see reviews by Ek et al. 2004; Hoppstock and Sures 2004; Zimmermann and Sures 2004; Zereini and Alt 2006; Haus et al. 2010) with focus on the biological availability, uptake and accumulation of platinum, palladium and rhodium by aquatic organisms. Unfortunately, field studies on the behaviour of traffic related PGE in the aquatic biosphere are very rare (Rauch and Morrison 1999; Moldovan et al. 2001; Haus et al.

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2007; Ruchter 2012) and are summarized in Ruchter et al. in this book. Therefore, the present article focuses solely on laboratory experiments and discusses the influence of different test parameters on metal uptake and bioaccumulation.

2 Uptake and Accumulation by Aquatic Plants

There is only a small number of publications on laboratory studies dealing with the uptake and accumulation of Pt, Pd and Rh by aquatic plants. An overview is given in Table 1. All investigations were performed with soluble inorganic chlorine compounds. Freshwater species as well as marine species were used as test organisms.

Investigations on the water hyacinth *Eichhornia crassipes* revealed that the bioaccumulation of Pt and Pd was one order of magnitude higher in the roots as compared with the shoots, whereas for Rh no significant differences occurred between the two plant parts (Farago and Parsons 1994). Farago and Parsons (1983) demonstrated that metal accumulation in the water hyacinth decreased in the order: Pt(II) > Pd(II) > Os(IV) = Ru(III) > Ir(III) = Rh(III), whereas Pd(II) removal within 180 min from seawater by *Ulva lactuca* was one order of magnitude higher compared to Pt(II) and Pt(IV) (Cosden et al. 2003). It is, however, unclear whether the platinum removal is only due to metal uptake by the plants or if and to which degree adsorption processes at container walls and plant surfaces may account for the reduction. In a 24 h-exposure study with the marine microalga *Chlorella stigmatophora* extra-cellular or adsorbed PGE were extracted from the plant samples by EDTA before metal analysis and the authors concluded from their results that Pd (II) was internalized to a considerably higher extent than Rh(III) and Pt(IV) although the extent of accumulation (sum of metal concentration in the EDTA extract and in the plant sample after extraction) was in the order: Rh > Pd ≫ Pt (Shams et al. 2013). However, after the exposure period was extended to 158 h, the degrees of both, internalization and accumulation, were greatest for Rh(III) and similar between Pd(II) and Pt(IV) (Shams et al. 2013). Studies on the distribution of PGE within plant cells are scarce. In the unicellular green alga *Pseudokirchneriella subcapitata* transmission electron microscopy (TEM) and proteomic analysis demonstrated that the main cellular target of Pd is the chloroplast (Vannini et al. 2011). Factors which may affect the bioaccumulation of Pt, Pd and Rh are discussed below.

3 Uptake and Accumulation by Aquatic Animals

As compared with plants more publications are available on the uptake and accumulation of Pt, Pd and Rh by aquatic animals. Table 2 gives an overview about the laboratory studies. Nearly all investigations were performed with freshwater

Table 1 Laboratory studies on the uptake and bioaccumulation of Pt, Pd and Rh by aquatic plants

Test organism	Exposure medium	Metal source	Exposure concentration	Exposure period	Reference
Periphyton community	Filtered (<0.2 µm) stream water or reference water	$Na_2Pt(II)Cl_4 \times 4\ H_2O$ $Na_2Pt(IV)Cl_6 \times 6\ H_2O$	10^{-9} bis 10^{-6} mol/L	23.5 h	Rauch et al. (2004)
Pseudo-kirchneriella subcapitata	Algal culture medium	K_2PdCl_4	0.03, 0.075, 0.15 mg/L	72 h	Vannini et al. (2011)
Fontinalis antipyretica	Distilled water	H_2PtCl_6	50, 200 µg/L	25 d	Veltz et al. (1994)
Eichhornia crassipes	Half-strength nutrient solution	cis-$PtCl_2(NH_3)_2$	0.05, 0.5, 2.5, 10 mg/L	2 w	Farago and Parsons (1994)
		trans-$PtCl_2(NH_3)_2$	0.05, 0.5, 2.5, 10 mg/L		
		K_2PtCl_4, $PtCl_4$, $(NH_4)_2PtCl_6$	0.05, 0.5, 2.5, 10 mg/L		
		K_2PdCl_4 cis-$PdCl_2(NH_3)_2$	0.05, 0.5, 2.5, 10 mg/L		
		Na_3RhCl_6	0.05, 0.5, 2.5, 10, 20, 30 mg/L		
Eichhornia crassipes		Soluble salts			Farago and Parsons (1983)
Elodea canadensis	Sigma® Bold modified basal nutrient solution, ± humic acid, ± Ca, ± Zn	Pt(IV) (standard)	0.05, 0.1, 1.0, 5.0 mg/L	2 w	Diehl and Gagnon (2007)
		Pt(IV), Pd(II), Rh(III) (multi-standard)	0.1 mg/L each		
Chlorella stigmatophora	Sea water enriched with nutrients, trace metals, EDTA and vitamins (Guillard's f/2 formulation)	Pt(IV), Pd(II), Rh(III) (standards)	20 µg/L each	24 h, 156 h	Shams et al. (2013)

(continued)

Table 1 (continued)

Test organism	Exposure medium	Metal source	Exposure concentration	Exposure period	Reference
Ulva lactuca	Natural seawater (filtered < 0.2 µm)	Pt(IV), Pd(II) (standards)	1.0 µM Pd + 0.5 µM Pt	≤ 180 min	Cosden et al. (2003)
		$K_2Pt(II)Cl_4$, $Pt(IV)Cl_2$, Pd(II)Cl_2	5.0 µM each		
Ulva lactuca	Natural sea water (filtered < 5 µm)	Pt(IV), Pd(II), Rh(III) (standards)	10 µg/L each	≤ 100 h	Turner et al. (2007)
Ulva lactuca	Synthetic seawater, salinity (S15–35), ± humic substances	Pd(II) (standard)	10.6 µg/L	24 h	Turner et al. (2008)
Ulva lactuca	Natural sea water (filtered <5 µm), ± surfactants	Pd(II) (standard)	5-30 µg/L	24 h	Masakorala et al. (2008)
Ulva lactuca	Natural sea water (filtered <0.6 µm), "estuarine" water, distilled water	cis-$PtCl_2(NH_3)_2$	10, 25, 50, 100, 150 nM	≤ 48 h	Easton et al. (2011)

Exposure concentrations are given as nominal concentrations of Pt, Pd or Rh, except for particulate metal sources

Table 2 Laboratory studies on the uptake and bioaccumulation of Pt, Pd and Rh by aquatic animals

Test organism	Exposure medium	Metal source	Exposure concentration	Exposure period	Reference
Annelids					
Lumbriculus variegatus	Distilled water	Pt chloride	50, 100, 200, 300, 400 µg/l	6 d 34 d (for 50 µg/L)	Veltz et al. (1994)
Lumbriculus variegatus	Distilled water	H_2PtCl_6	0.05 mg/L	30 d	Veltz et al. (1996)
Arenicola marina	Estuarine water (made of filtered seawater and Milli-Q water)	Pt(IV), Pd(II) (standards) ground catalyst material (150 µg/g Pt, 0.55 µg/g Pd)	40 ppb 8 g catalyst/L	10 d	French and Turner (2008)
Crustacea					
Asellus aquaticus	Nanopure water	Pt (standard)	50, 100, 200, 1,000 µg/L	96 h	Rauch and Morrison (1999)
		$Na_2Pt(II)Cl_4$ $H_2Pt(IV)Cl_6$	0.1 mg/L	96 h	
Asellus aquaticus	Nanopure water	Pt, Pd, Rh (single and multi-standards)	5, 25, 100, 500 µg/l	24 h	Moldovan et al. (2001)
		River sediment (10 ng/g Pt, 0.7 ng/g Rh) Tunnel dust (55 ng/g Pt, 10 ng/g Rh) Road dust (4 ng/g Pt, 2.8 ng/g Rh) Road dust (157 ng/g Pt, 60 ng/g Rh)	10 g sediment/L 4 g tunnel dust/L 5 g road dust/L	24 h, 96 h	
		Ground catalyst materials (Nist SRM-2557: 1131 µg/g Pt, 233 µg/g Pd, 135 µg/g Rh IMEP-11: 2155 µg/g Pt, 444 µg/g Rh)	360 mg catalyst/L	24 h	

(continued)

Table 2 (continued)

Test organism	Exposure medium	Metal source	Exposure concentration	Exposure period	Reference
Mollusca					
Littorina littorea	Natural sea water (filtered < 0.6 µm)	Pt(IV), Pd(II), Rh(III) (multi-standard)	20 mg/L (each)	5 d	Mulholland and Turner (2011)
Marisa cornuarietis	Tap water	Pt (standard)	0.1, 1, 10, 50, 100 µg/L	14 d	Osterauer et al. (2009)
Marisa cornuarietis	Tap water	Pt (standard)	100, 200 µg/l	26 d	Osterauer et al. (2010)
Corbicula sp.	Non chlorinated tap water	Pt(IV) (standard)	0.01, 0.05, 0.1, 100 µg/L	70 d	Ruchter (2012)
Dreissena polymorpha	Non chlorinated tap water	Pt(IV), Pd(II), Rh(III) (standards)	500 µg/L	10 weeks	Singer et al. (2005)
Dreissena polymorpha	Non chlorinated tap water	Pd(II) (standard)	0.05, 5, 50, 500 µg/L	10 weeks	Frank et al. (2008)
Dreissena polymorpha	Non chlorinated tap water, Humic water of a bog lake, Humic water + Ca	$PtCl_4$ $PdSO_4$ $RhCl_3$ *3 H_2O	100 µg/L 100 µg/L 100 µg/L	28 d	Sures and Zimmermann (2007)
Dreissena polymorpha	Non chlorinated tap water Humic water of a bog lake	Ground catalyst materials (cat 1: 2.41 mg/g Pt, <0.04 mg/g Pd, 0.60 mg/g Rh cat 2: <0.04 mg/g Pt, 2.66 mg/g Pd, and 0.61 mg/g Rh)	100 mg cat 1/L + 100 mg cat 2/L	18 weeks	Zimmermann et al. (2005a)
Dreissena polymorpha	Non chlorinated tap water	Road dust (244 ng/g Pt, 29 ng/g Pd, 26 ng/g Rh)	100 g road dust/L	26 weeks	Sures et al. (2002)

(continued)

Table 2 (continued)

Test organism	Exposure medium	Metal source	Exposure concentration	Exposure period	Reference
Dreissena polymorpha	Non chlorinated tap water Humic water of a bog lake	Road dust (244 ng/g Pt, 29 ng/g Pd, 26 ng/g Rh)	100 g road dust/L	26 weeks	Zimmermann et al. (2002)
Fish					
Danio rerio		H_2PtCl_6	16 µg/l	2, 7, 14 d	Jouhaud et al. (1999a, b)
Danio rerio	Reconstituted water (OECD guideline 203)	Pt (standard)	0.1, 1, 10, 50, 100 µg/L	96 h	Osterauer et al. (2009)
Anguilla anguilla	Non chlorinated tap water Humic water of a bog lake	$PtCl_4$,	170 µg/l Pt	6 w	Zimmermann et al. (2004)
		$RhCl_3$ *3 H_2O	260 µg/L Rh		
Anguilla anguilla	Non chlorinated tap water	Ground catalyst material (0.36 mg/g Pt, 4.98 mg/g Pd, 0.36 mg/g Rh)	200 mg catalyst/L	6 w	Zimmermann et al. (2005b)
Anguilla anguilla	Non chlorinated tap water	Ground catalyst material (1.21 mg/g Pt, 0.61 mg/g Rh)	200 mg catalyst/L	6 w	Sures et al. (2003)
Anguilla anguilla	Non chlorinated tap water	Road dust (101 ng/g Pt, 21 ng/g Pd, 19 ng/g Rh)	100 g road dust/L	4 w	Sures et al. (2001)
Barbus barbus	Well water	Ground catalyst material (2.36 mg/g Pt, 2.36 mg/g Pd, 0.47 mg/g Rh)	100 mg catalyst/L	4 w	Sures et al. (2005a, b)
Squalius cephalus	Non chlorinated tap water	Pt(IV) (standard)	100 µg/L	7, 13, 21, 28, 35 d	Ruchter (2012)
Amphibia					
Xenopus laevis	FETAX solution	$(NH_4)_2PtCl_4$ $(NH_4)_2PtCl_6$	0.08, 0.4, 2, 10, 50 µM	112 h	Monetti et al. (2003)
Acanthocephala (parasites)					
Paratenuisentis ambiguus	Non chlorinated tap water	Ground catalyst material (1.21 mg/g Pt, 0.61 mg/g Rh)	200 mg catalyst/L	6 w	Sures et al. (2003)

(continued)

Table 2 (continued)

Test organism	Exposure medium	Metal source	Exposure concentration	Exposure period	Reference
Paratenuisentis ambiguus	Non chlorinated tap water	Ground catalyst material (0.36 mg/g Pt, 4.98 mg/g Pd, 0.36 mg/g Rh)	200 mg catalyst/L	6 w	Zimmermann et al. (2005b)
Pomphorhynchus laevis	Well water	Ground catalyst material (2.36 mg/g Pt, 2.36 mg/g Pd, 0.47 mg/g Rh)	100 mg catalyst/L	4 w	Sures et al. (2005a, b)
Pomphorhynchus laevis	Non chlorinated tap water	Pt(IV) (standard)	100 µg/L	13, 28 d	Ruchter (2012)
Pomphorhynchus tereticollis	Non chlorinated tap water	Pt(IV) (standard)	100 µg/L	7, 21, 35 d	Ruchter (2012)

Exposure concentrations are given as nominal concentrations of Pt, Pd or Rh, except for particulate metal sources.

species, except for one study with the marine snail *Littorina littorea* (Mulholland and Turner 2011) and a marine microcosm study using the polychaete *Arenicola marina* (French and Turner 2008). The uptake of PGE was demonstrated for different species of annelids, crustaceans, molluscs, fish and intestinal fish parasites. In most studies soluble inorganic chlorine compounds were used as metal source. Only a few experiments dealt with particle-bound PGE and/or environmental materials such as ground catalyst material, river sediment, and tunnel or road dust of heavily frequented roads. The uptake of Pt, Pd and Rh by animals was verified for all metal sources tested.

In crustaceans such as *Asellus aquaticus*, the highest percentage of the total platinum was found in the exoskeleton (Rauch and Morrison 1999). In contrast, the shell of marine snails exposed to Pt, Pd and Rh showed rather low metal levels as compared with other compartments such as visceral complex, head, foot, gill, stomach and kidney (Mulholland and Turner 2011). In fish, liver and kidney are the main target organs of PGE accumulation (Sures et al. 2001; Zimmermann et al. 2004, 2005b) although studies with barbel (*Barbus barbus*) and European eel (*Anguilla anguilla*) demonstrated also considerable levels of Pt, Pd and Rh in gills and intestinal wall (Sures et al. 2005a, b; Zimmermann et al. 2004). Additionally, elevated metal concentrations were found in the bile liquid (Pt and Rh) and spleen (only Rh) of the exposed eels (Zimmermann et al. 2004). The varying degree of bioaccumulation in different animal species is discussed later in the paragraph “Test organism”.

4 Test Parameters Affecting the Results of Aquatic Exposure Studies

Laboratory studies on the uptake and accumulation of PGE by aquatic organisms were performed under various conditions. The influence of these test parameters (see Fig. 1) on uptake and accumulation of PGE by biota is discussed within this chapter.

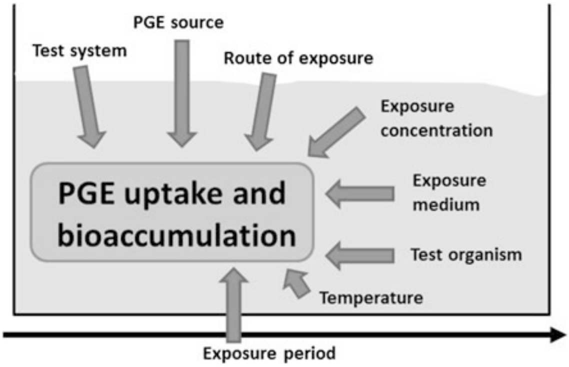

Fig. 1 Parameters of laboratory exposure studies affecting the PGE uptake and bioaccumulation by aquatic organisms

4.1 Test System

In all published investigations static tests (without water replacement) or semi-static tests (with replacements of the water at intervals) were performed. Accordingly, exposure concentrations in the water generally range between a maximum directly after metal addition and a minimum just before water replacement or at the end of exposure (e.g. Zimmermann et al. 2004; Singer et al. 2005; Sures and Zimmermann 2007; Frank et al. 2008). Only flow-through systems can guarantee for a more or less constant aqueous metal concentration. From different experiments with zebra mussels exposed to soluble PGE it can be concluded that in static tests the accumulation plateau is reached within a shorter exposure period as compared with semi-static tests (Singer et al. 2005; Sures and Zimmermann 2007; Frank et al. 2008) which clearly indicates that the frequency of water replacement influences the accumulation kinetics.

Furthermore, the exposure container material can affect PGE concentrations in the water. Numerous aquatic exposure studies showed that the quantified aqueous PGE concentration is far below the metal concentration applied (e.g. Singer et al. 2005; Sures and Zimmermann 2007; Frank et al. 2008). Sures and Zimmermann (2007) demonstrated in an experiment in which zebra mussel shells were exposed to soluble PGE the same way as alive zebra mussels that metal loss in the tank water is due to abiotic processes. Cobelo-Garcia et al. (2007) showed in an investigation with Pt(IV), Pd(II) and Rh(III) that the greatest adsorptive and/or precipitative loss was obtained for low-density polyethylene and the least loss for borosilicate glass. Accordingly, the material of the tanks used for exposure studies may have an important influence on the biological availability and consequently on the bioaccumulation of PGE. Thus, adsorption processes justify the need to analyse aqueous metal levels during the whole exposure period instead of solely presenting nominal concentrations which are often up to ten times higher than the real aqueous levels (Sures and Zimmermann 2007).

Generally, aquatic tests on the bioaccumulation of PGE were performed without sediments although in natural aquatic ecosystems sediments including their inhabitants may have an important impact on the biological availability of PGE to organisms. For example, biotransformation by bacteria may lead to altered biological availability of the PGE. The only information on the effect of sediment on the bioaccumulation of PGE comes from a marine microcosm study with Pt(IV) and Pd(II) in which the Pt concentrations were higher in polychaetes from tubes without sediment as compared with those from tubes with sediment, whereas opposite results were found for Pd (French and Turner 2008).

Fluctuating PGE concentrations in the water during an experiment and the increased time to reach steady-state condition in semi-static tests can cause problems in determination of bioaccumulation factors which are discussed later.

4.2 PGE Sources

Metal source or metal speciation can considerably influence biological availability. As shown in experiments with zebra mussels bioaccumulation of soluble PGE is a rather fast process compared with the very slow bioaccumulation of particle bound PGE (Sures and Zimmermann 2007). It seems reasonable, that soluble PGE show a greater biological availability than particle-bound PGE. This was demonstrated in different experiments with zebra mussels exposed to soluble PGE, ground catalyst material or road dust. Although the exposure periods were different in the three experiments, the bioaccumulation factors showed the following tendency: soluble PGE > catalyst material > road dust (Fig. 2). Also French and Turner (2008) found a greater assimilation efficiency of Pt in polychaetes when the metal was applied in soluble form as compared with catalyst material. However, in the same experiment the assimilation efficiency for Pd was very similar for soluble and particle-bound Pd (French and Turner 2008). Concerning particle-bound PGE, bioaccumulation in asellids exposed to catalyst material was three orders of magnitude higher as compared to exposure with environmental PGE sources, and Pt accumulation was higher in asellids exposed to river sediments as compared with tunnel dust (Moldovan et al. 2001).

With respect to different soluble Pt species, Pt uptake by *A. aquaticus* was found to be higher for Pt(IV) than for Pt(II) (Rauch and Morrison 1999). In contrast, zebra mussels as well as frog embryos demonstrated a significant higher uptake of Pt(II) as compared with Pt(IV) (Zimmermann 2002; Monetti et al. 2003).

In some exposure studies test organisms were simultaneously exposed to Pt, Pd and Rh. Similar accumulation results were obtained for asellids and zebra mussels

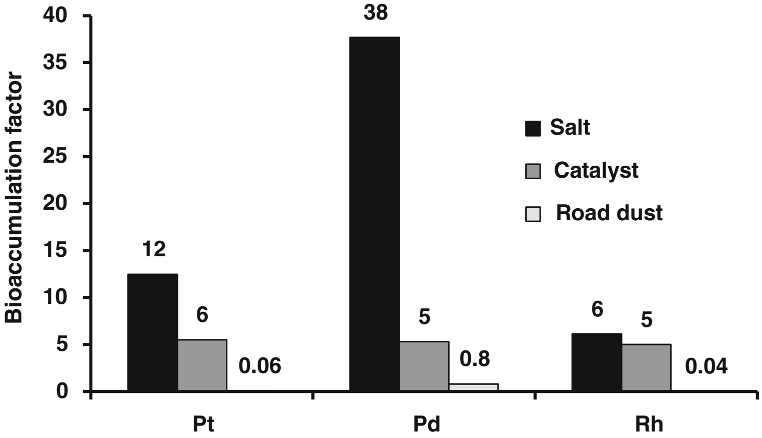

Fig. 2 Bioaccumulation factors ($c_{\text{mussel}}/c_{\text{water, nominal}}$) for zebra mussels *Dreissena polymorpha* exposed to soluble PGE for 4 weeks, catalyst material for 18 weeks or road dust for 26 weeks. For details see Zimmermann et al. (2002, 2005a) and Sures and Zimmermann (2007)

exposed to individual or combined standard solutions of Pt, Pd and Rh (Moldovan et al. 2001; Zimmermann 2002) although Pt uptake by *E. canadensis* was found to be higher in the presence of Pd and Rh (Diehl and Gagnon 2007).

Additionally, the PGE source can affect the routes of uptake. For example, the size of the PGE-particles and/or the binding strength of the metals to foodstuff can enhance PGE uptake via ingestion. Particle characteristics are of special significance for filter feeding organism such as mussels (Ward and Shumway 2004). But also for asellids it can be assumed that PGE from catalyst material were taken up as particles as accumulated PGE ratios in the asellids were similar to those in the catalyst material (Moldovan et al. 2001).

4.3 Route of Exposure

Usually, PGE were applied via the exposure medium in aquatic exposure studies. If test organisms were fed, PGE adsorption to food and subsequent oral uptake of contaminated food is possible. Binding of PGE to food particle is again dependent on the PGE speciation (see above). Thus, all zebra mussel exposure studies were performed without feeding the animals to avoid uncontrolled dietary uptake of metals adsorbed to food particles (for references see Table 2). However, as zebra mussels are able to absorb dissolved organic carbon (DOC) and most probably also metals bound therein (Roditi et al. 2000), it can be assumed that dietary PGE uptake is combined with aqueous PGE uptake in exposure studies using humic water (Sures and Zimmermann 2007). Also if particle-bound PGE are used for exposure, both uptake routes appear to be possible. In summary, the specific combination of metal source and exposure medium affects the route of uptake and niveau of bioaccumulation.

To investigate the effects of exposure routes, the marine snail *Littorina littorea* was exposed to PGE in three different treatments: PGE dissolved in sea water, PGE in seawater and food, and PGE only in food (Mulholland and Turner 2011). Mulholland and Turner concluded from their results that diet is the most important way for accumulation of Rh and Pd, while accumulation of Pt appears to proceed mainly from the aqueous phase. French and Turner (2008) suggested from results of a microcosm study with the polycheate *Arenicola marina* that both aqueous and dietary sources were important for Pt and Pd bioaccessibility in the sediment.

4.4 Exposure Concentration

Exposure concentrations should be high enough to allow for a reliable quantification of the PGE in the test organisms, but simultaneously ranging below the threshold at which severe biological effects are expected. Additionally, it would be preferable if exposure concentrations are in the same range as real environmental contaminations. As usually environmental levels are rather low, higher concentrations are applied under laboratory conditions in order to overcome analytical limits.

It was shown in several exposure studies with soluble PGE that Pt concentrations in the test organisms increased with the exposure concentration and no metal saturation was observed within the tested concentration ranges (see Tables 1, 2). This was demonstrated for water plants such as microalgae (Rauch et al. 2004), *Eichhornia crassipes* (Farago and Parsons 1994), *Elodea canadensis* (Diehl and Gagnon 2007) and *Fontinalis antipyretica* (Veltz et al. 1994) as well as for aquatic animals such as *Lumbriculus variegatus* (Veltz et al. 1994), *Asellus aquaticus* (Rauch and Morrison 1999), *Corbicula* sp. (Ruchter 2012), *Dreissena polymorpha* (Zimmermann 2002), *Marisa cornuarietis* (Osterauer et al. 2009) and *Danio rerio* (Osterauer et al. 2009). A similar trend was also found for the Pd and Rh uptake in *E. crassipes* (Farago and Parsons 1994) and *D. polymorpha* (Zimmermann 2002; Frank et al. 2008).

4.5 Exposure Medium

Various exposure media with different physical and chemical properties were used for aqueous exposure studies. The effect of different parameters such as salinity, presence of dissolved organic matter or presence of inorganic ions on bioaccumulation of PGE was investigated in several laboratory studies. Cobelo-Garcia et al. (2007) studied the influence of the water type (artificial and native fresh- and seawater) over a wide pH range on the adsorptive and precipitative loss of Pt(IV), Pd(II) and Rh(III) in the water. The results showed that Pd(II)-recovery was enhanced in seawater as compared with freshwater which is explained by its complexation with chloride, whereas the loss of Rh(III) significantly increased in seawater mainly due to precipitation. For Pt(IV) the recovery was generally higher than 90 % in seawater whereas in freshwater the recovery was in some cases lower dependent on the container material and pH (Cobelo-Garcia et al. 2007). In contrast, an exposure study on the Pd uptake by the marine alga *U. lactuca* showed no effect on the PGE uptake over a wide salinity range (15–35 ‰, Turner et al. 2008).

In some studies the effect of dissolved organic matter on the biological availability, uptake and accumulation of soluble PGE was investigated. Cobelo-Garcia et al. (2007) demonstrated that the presence of natural dissolved organic matter in freshwater increases the recovery of Pd(II) and Rh(III) in the water but enhances the loss of Pt(IV). The same trends were found in the water of an exposure study with zebra mussels where the use of humic water from a bog lake was compared with the use of tap water as exposure medium (Sures and Zimmermann 2007).

Concerning plants, the addition of humic acids to the nutrient solution increased the Pt accumulation in *E. canadensis* up to a factor of 2 as compared with the humic-free Pt treatment (Diehl and Gagnon 2007). This enhancement of the metal accumulation was investigated over a pH range of 5–8 and was found to be highest at a pH of 8. Also Rauch et al. (2004) found differences in the uptake of Pt by periphyton communities maintained in two different water types which mainly varied in the occurrence of organic ligands. However, for the marine macroalga *U. lactuca* the addition of humic substances to seawater resulted in a small suppression of Pd uptake as compared with the humic-free system (Turner et al. 2008).

Also the bioaccumulation of soluble PGE in aquatic animals was influenced by the presence of humic substances in the water. Sures and Zimmermann (2007) demonstrated that after 4 weeks of exposure the bioaccumulation of Pd in the mussel soft tissue was significantly higher in tap water as compared with humic water, whereas Rh showed the opposite trend and no effect of the water type occurred on the Pt accumulation. This phenomenon is explained by the binding of the three different PGE to different fractions of humic substances which vary in their aqueous solubility and their biological availability for the mussels (Sures and Zimmermann 2007). In contrast, Pt was accumulated in different tissues of eels to a higher extend when the eels were maintained in tap water as compared with humic water (Zimmermann et al. 2004).

Furthermore, humic substances can increase the solubility of metallic Pt and Pd (Lustig et al. 1998; Bowles and Gize 2005). Correspondingly, in experiments using catalyst material or road dust as metal source a clearly higher uptake of Pt, Pd and Rh was found for mussels maintained in humic water as compared with tap water (Zimmermann et al. 2002, 2005a, b).

In contrast to natural complexing agents, Masakorala et al. (2008) found no measurable influence of two synthetic surfactants (sodium dodecyl sulphate and Triton X-100) on the internalisation of Pd by *U. lactuca*, however, the presence of HDTMA (hexadecyltrimethylamonnium bromide) had a decreasing impact.

The effect of the presence of divalent cations on the PGE uptake in *E. canadensis* was studied by Diehl and Gagnon (2007). They demonstrated that addition of Ca^{2+} or Zn^{2+} to the nutrition solution resulted in an enhanced Pt accumulation in the aquatic plant. Similarly, addition of $CaCl_2$ to humic water increased the Pt accumulation in zebra mussels whereas the accumulation of Pd and Rh remained unaffected (Sures and Zimmermann 2007).

These examples show that different water or medium parameters can affect the biological availability of PGE. Consequently, comparisons between exposure studies using different water types are problematic. Thus, in respect of comparability and reproducibility the use of standardized water according to international guidelines (e.g. OECD, ASTM) is recommended. However, with the use of natural water the laboratory conditions better resemble to field situations.

4.6 Exposure Period

Generally, the course of PGE uptake comprises a period of rising metal concentrations with subsequent transition to an accumulation plateau (Fig. 3, Sures and Zimmermann 2007). Determination of bioaccumulation factors presumes that the accumulation plateau is reached (see below). The time needed to reach the

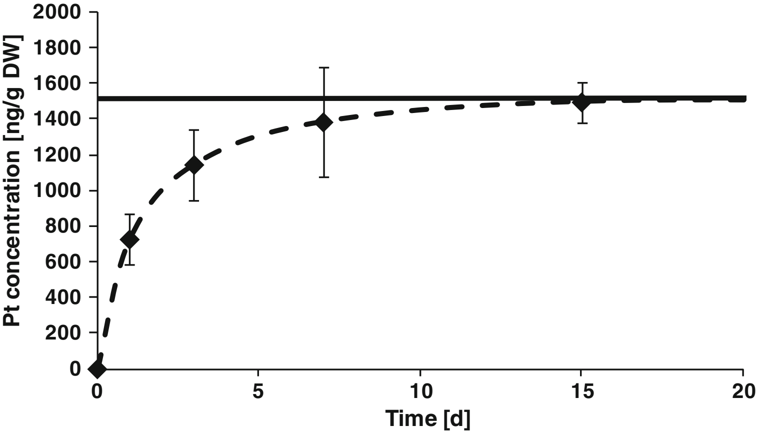

Fig. 3 Course of Pt uptake in the soft tissue (*DW* dry weight) of *Dreissena polymorpha* exposed to non-chlorinated tap water containing $PtCl_4$ (100 μg/L Pt). Error bars represent standard deviations. For details see Sures and Zimmermann (2007)

accumulation plateau depends on various parameters such as metal source, test system and test organism.

In a static mussel exposure experiment with soluble PGE the accumulation plateau was reached approximately after 2 weeks of exposure whereas in a comparable study with ground catalyst material the PGE concentrations in the mussels increased over the whole exposure period of 18 weeks (Zimmermann et al. 2005a, b, Sures and Zimmermann 2007). However, in a semi-static test system with soluble PGE and water replacement twice a week, the concentration of Pt, Pd and Rh in *D. polymorpha* did not reach the accumulation plateau after 10 weeks of exposure (Singer et al. 2005; Frank et al. 2008).

Due to these differences, it is recommended to record the time-dependent course of the PGE concentrations in the test organisms to be sure that the accumulation plateau is reached. On the other hand, for kinetic investigations a higher number of test individuals is required. This may cause problems in animal tests in which animal care aspects have to be considered.

4.7 Test Organism

The organisms used so far in bioaccumulation studies are listed in Tables 1 and 2. Important criteria for choosing a test species are among others availability in sufficient quantities, easy maintenance under laboratory conditions and in respect of environmental aspects also their representative role in the structure and function of ecosystems.

A comparison of the accumulation potential of different test organisms investigated in various experiments is difficult as the calculation of bioaccumulation factors bears some problems (see below). However, it is obvious, that the behavioural pattern, the way of life and the habitat of the test organism will have an important effect on the uptake of PGE in aquatic systems.

Concerning aquatic animals, acanthocephalans, a group of parasites living in the intestine of their definitive fish host, demonstrated an exceptional accumulation potential for Pt, Pd and Rh. For example, the parasites *Pomphorhynchus laevis*, *Pomphorhynchus tereticollis* and *Parateniusentis ambiguus* accumulated PGE to considerably higher degrees than the respective fish hosts (Sures et al. 2003, 2005a, b, Zimmermann et al. 2005b, Ruchter 2012). This phenomenon was also reported for other metals (Sures 2004). Furthermore, Ruchter (2012) demonstrated that Pt concentrations in liver and intestine of chub were higher in uninfected individuals than in individuals infected with *P. tereticollis*. Thus, parasites can even reduce metal accumulation in their fish host (Sures 2008).

Rauch and Morrison (1999) demonstrated that the Pt concentration in the moulted exoskeleton of *A. aquaticus* was considerably higher than the concentration in whole asellids. Consequently, the moulting status of *A. aquaticus* and other crustaceans may have an influence on the PGE bioaccumulation determined in the entire organism.

Also the number of individuals or the biomass present in the test container may affect bioaccumulation in the test organism. This was shown in a 24-h exposure study with *C. stigmatophora* where the bioaccumulation of Pt, Pd and Rh decreased with increasing cell density (Shams et al. 2013).

Additionally, the metal uptake by the test organism may be overestimated due to adsorbed metals at the surface of the test organisms and/or metals present in the gut or digestive system which are not yet internalized. For example, platinum in the exoskeleton of *A. aquaticus* was found to represent 60–90 % of the total platinum in the animal before depuration and 60–70 % after depuration (Rauch and Morrison 1999). In *Lumbriculus variegatus* previously exposed to soluble Pt over 30 days the Pt concentration decreased by about 70 % after 4 days of decontamination (Veltz et al. 1996). However, Sures and Zimmermann (2007) determined the concentrations of Pt, Pd and Rh in soft tissues of zebra mussels as a function of the depuration period following 4-week exposure to soluble PGE and found no significant differences in the PGE concentrations of the mussels sampled after 5-min depuration and after 3-day depuration.

4.8 Temperature

It is generally known that temperature affects the reaction rate of chemicals. Most aquatic animals are poikilothermic which means that their body temperature varies with the ambient water temperature. Consequently, it can be assumed that the bioaccumulation of PGE at least in poikilothermic aquatic organisms is influenced by temperature. This was demonstrated in an experiment with *Lumbriculus variegatus* exposed to Pt at 4 °C and at 20 °C showing that the bioaccumulation of Pt decreased at lower temperature (Veltz et al. 1994, 1996).

5 Bioaccumulation Factors

Bioaccumulation factors are often used to compare the bioaccumulation of different test species or different metals. The bioaccumulation factor (BAF) is calculated as the ratio of the metal concentration in the test organism to the metal concentration in the water.

If the test organisms for exposure studies originally derived from the field, it is recommended to compensate for their background contamination by subtraction of the PGE concentrations of the unexposed controls from that of the exposed individuals (Zimmermann et al. 2002). Determination of bioaccumulation factors assumes that the accumulation plateau in the test organism is reached (see Fig. 3). That means that the exposure period of the laboratory test is adequate (see above).

Often the nominal water concentration is used to calculating the BAF although the bioavailable aqueous concentration is often much lower for the reasons mentioned above. In most experiments a static or semi-static test system is used, so that the applied concentration is not constant during the whole exposure period. Therefore, Sures and Zimmermann (2007) used in a static test system for the determination of the BAF the weighted average aqueous concentration which was calculated from the PGE concentrations quantified at different intervals during a 4-week exposure. A similar mathematic approximation was done in a semi-static experiment with two water replacements over an entire exposure period of 6 weeks (Zimmermann et al. 2004). In a semi-static test system Singer et al. (2005) calculated two BAFs by using the mean quantified metal concentration in the tank water before and after water replacement, respectively.

Furthermore, the water samples were often filtered (<0.45 µm) before metal quantification, so that only the dissolved metal fraction was used for the calculation of the BAF (e.g. Zimmermann et al. 2004, Singer et al. 2005, Sures and Zimmermann 2007). However, in laboratory studies in which mussels were exposed to particle-bound PGE (e.g. ground catalyst material or road dust) the BAF was determined by using the nominal metal level in the water (Zimmermann et al. 2002, 2005a). This is reasonable as mussels are able to feed on particles.

Due to all the reasons discussed above it is highly recommended to carefully consider how the BAF is determined and to compare BAFs of different studies only with special care. Nevertheless, BAFs for different metals determined in the same exposure study have a good comparability. For example, for asellids exposed to soluble PGE the BAF decreased in the order Pd > Pt > Rh (Moldovan et al. 2001). Also in mussels Pd showed the highest BAF whereas the BAFs for Pt and Rh were similar (Sures and Zimmermann 2007). Furthermore, Zimmermann et al. (2002) compared the BAFs of Pt, Pd and Rh with other metals in mussels exposed to road dust and found the following order: Cu > Cd > Ag > Pd > Sb > Pb > Fe > Pt > Rh. However, in a comparable exposure study with catalyst material the mussels exhibited a similar BAF for all three PGE (Zimmermann et al. 2005a).

Other measures for biological availability, uptake and bioaccumulation found in literature are the assimilation efficiency (AE) and different constants defining the partitioning between the test organism and its ambient environment (French and Turner 2008). Additionally, uptake rates were obtained by linear regression between the metal concentration in the test organism and the exposure concentration (Rauch et al. 2004) or the exposure time (Zimmermann et al. 2005a). But also these measures should be used with care in order to compare results of different studies.

6 What Can We Learn from Laboratory Studies?

The laboratory studies demonstrated a clear biological availability, uptake and bioaccumulation of Pt, Pd and Rh deriving from soluble as well as particulate metal sources for aquatic plants and animals. The similar results of exposure experiments with a single PGE as compared with multiple PGE exposure indicate that there is no competition between Pt, Pd and Rh for the same uptake mechanisms. Generally, uptake of soluble PGE is quicker compared with particle-bound PGE from e.g. catalyst material or road dust. An exposure study with road dust demonstrated that the bioaccumulation of PGE is in the range of other (heavy) metals (Zimmermann et al. 2002).

The three metals (Pt, Pd and Rh) exhibited a different behaviour in the aquatic biosphere. Laboratory studies helped to discover several factors which affect the biological availability and bioaccumulation in aquatic organisms, e.g. presence of humic substances, metal speciation, route of exposure, exposure period and concentration, temperature and infection of the test organisms with parasites.

For a better understanding of the environmental situation it is important to know the effects discussed above in this chapter. In natural aquatic ecosystems further factors not yet investigated may play an important role, e.g. the transfer of PGE within food webs. Aquatic ecosystems are complex structures with permanent fluctuations in their environmental conditions and in the mixture of chemicals biologically available in the water. Furthermore, in nature organisms are chronically exposed to lower metal concentrations as compared with most laboratory studies. But due to analytical limits in the determination of Pt, Pd and Rh in biological samples exposure concentrations are generally far above real field situations. Due to these reasons the transfer of laboratory results to field conditions bears a lot of difficulties.

Although further research is necessary for a comprehensive understanding of the behaviour of PGE in aquatic ecosystems, the present laboratory results already deliver valuable information to understand the basics of PGE uptake and bioaccumulation by aquatic organisms.

References

Bowles J, Gize A (2005) A preliminary study of the release of platinum and palladium from metallic particles in the surface environment by organic acids: relevance to weathering of particles. Mineral Mag 69:687–693

Cobelo-Garcia A, Turner A, Millward GE, Couceiro F (2007) Behaviour of palladium (II), platinum (IV), and rhodium (III) in artificial and natural waters : Influence of reactor surface and geochemistry on metal recovery. Anal Chim Acta 585:202–210

Cosden JM, Schijf J, Byrne RH (2003) Fractionation of platinum group elements in aqueous systems: Comparative kinetics of palladium and platinum removal from seawater by *Ulva lactuca* L. Environ Sci Technol 37:555–560

Diehl DB, Gagnon ZE (2007) Interactions between essential nutrients with platinum group metals in submerged aquatic and emergent plants. Water Air Soil Pollut 184:255–267

Easton C, Turner A, Sewell G (2011) An evaluation of the toxicity and bioaccumulation of cisplatin in the marine environment using the macroalga, *Ulva lactuca*. Environ Pollut 159:3504–3508

Ek KH, Morrison GM, Rauch S (2004) Environmental routes for platinum group elements to biological materials – a review. Sci Total Environ 334–335:21–38

Farago ME, Parsons PJ (1983) The uptake and accumulation of platinum metals by the water hyacinth (*Eichhornia crassipes)*. Inorganica Chim Acta 79:233–234

Farago ME, Parsons PJ (1994) The effects of various platinum metal species on the water plant *Eichhornia crassipes* (Mart) Solms. Chem Spec Bioavailab 6(1):1–12

Frank SN, Singer C, Sures B (2008) Metallothionein (MT) response after chronic palladium exposure in the zebra mussel, *Dreissena polymorpha*. Environ Res 108:309–314

French B, Turner A (2008) Bioavailability of Pt and Pd in coastal sediments: the role of the Polychaete, *Arenicola marina*. Environ Sci Technol 42:3543–3549

Haus N, Zimmermann S, Sures B (2010) Precious metals in urban aquatic systems: platinum, palladium and rhodium: sources, occurrence, bioavailability and effects. In: Fatta-Kassinos D, Bester K, Kümmerer K (eds) Xenobiotics in the urban water cycle: mass flows, environmental processes, mitigation and treatment strategies, Environmental Pollution, vol 16. Springer, Berlin, pp 73–86

Haus N, Zimmermann S, Wiegand J, Sures B (2007) Occurrence of platinum and additional traffic related heavy metals in sediments and biota. Chemosphere 66:619–629

Hoppstock K, Sures B (2004) Platinum-Group Metals. In: Merian E, Anke M, Ihnat M, Stoeppler M (eds) Elements and their compounds in the environment. Wiley, Weinheim, Germany, pp 1047–1086

Jouhaud R, Biagianti-Risbourg S, Vernet G (1999a) Atteintes ultrastructurales intestinales induites par une concentration subléthale de platine chez le téléostéen Brachydanio rerio. Bull Soc Zool Fr 124:111–116

Jouhaud R, Biagianti-Risbourg S, Vernet G (1999b) Effets du platine chez Brachydanio rerio (Téléostéen, Cyprinidé). I. Toxicité aiguë; bioaccumulation et histopathologie intestinales. J Appl Ichthyol 15:41–48

Lustig S, Zang S, Beck W, Schramel P (1998) Dissolution of metallic platinum as water soluble species by naturally occurring complexing agents. Mikrochim Acta 129:189–194

Masakorala K, Turner A, Brown MT (2008) Influence of synthetic surfactants on the uptake of Pd, Cd and Pb by the marine macroalga, *Ulva lactuca*. Environ Pollut 156:897–904

Moldovan M, Rauch S, Gómez MM, Palacios MA, Morrison GM (2001) Bioaccumulation of palladium, platinum and rhodium from urban particulates and sediments by the freshwater isopod *Asellus aquaticus*. Water Res 35:4175–4183

Monetti C, Bernardini G, Vigetti D, Prati M, Fortaner S, Sabbioni E, Gornati R (2003) Platinum toxicity and gene expression in Xenopus embryos: analysis by FETAX and differential display. Altern Lab Anim 31:401–408

Mulholland R, Turner A (2011) Accumulation of platinum group elements by the marine gastropod *Littorina littorea*. Environ Pollut 159:977–82

Osterauer R, Haus N, Sures B, Köhler H (2009) Uptake of platinum by zebrafish (*Danio rerio*) and ramshorn snail (*Marisa cornuarietis*) and resulting effects on early embryogenesis. Chemosphere 77:975–982

Osterauer R, Marschner L, Betz O, Gerberding M, Sawasdee B, Cloetens P, Haus N, Sures B, Triebskorn R, Köhler H-R (2010) Turning snails into slugs: induced body plan changes and formation of an internal shell. Evol Dev 12:474–483

Rauch S, Morrison GM (1999) Platinum uptake by the freshwater isopod *Asellus aquaticus* in urban rivers. Sci Total Environ 235:261–268

Rauch S, Paulsson M, Wilewska M, Blanck H, Morrison GM (2004) Short-term toxicity and binding of platinum to freshwater periphyton communities. Arch Environ Contam Toxicol 47:290–296

Roditi HA, Fisher NS, Sanudo-Wilhelmy SA (2000) Field testing a metal bioaccumulation model for zebra mussels. Environ Sci Technol 34:2817–2825

Ruchter N (2012) Ecotoxicology of traffic related platinum in the freshwater environment. PhD thesis, University of Duisburg-Essen, Germany

Shams L, Turner A, Millward GE, Brown MT (2013) Extra- and intra-cellular accumulation of platinum group elements by the marine microalga, *Chlorella stigmatophora*. Water Res (published online doi:10.1016/j.watres.2013.10.055)

Singer C, Zimmermann S, Sures B (2005) Induction of heat shock proteins (hsp70) in the zebra mussel (*Dreissena polymorpha*) following exposure to platinum group metals (platinum, palladium and rhodium): comparison with lead and cadmium exposures. Aquat Toxicol 75:65–75

Sures B (2004) Environmental parasitology: relevancy of parasites in monitoring environmental pollution. Trends Parasitol 20:170–177

Sures B (2008) Host-parasite interactions in polluted environments. J Fish Biol 73:2133–2142

Sures B, Thielen F, Baska F (2005a) The intestinal parasite *Pomphorhynchus laevis* as a sensitive accumulation indicator for the platinum group metals Pt, Pd, and Rh. Environ Res 98:83–88

Sures B, Thielen F, Messerschmidt J, von Bohlen A (2005b) The intestinal parasite *Pomphorhynchus laevis* as a sensitive accumulation indicator for the platinum group metals Pt, Pd and Rh. Environ Res 98:83–88

Sures B, Zimmermann S (2007) Impact of humic substances on the aqueous solubility, uptake and bioaccumulation of platinum, palladium and rhodium in exposure studies with *Dreissena polymorpha*. Environ Pollut 146:444–451

Sures B, Zimmermann S, Messerschmidt J, von Bohlen A, Alt F (2001) First report on the uptake of automobile catalyst emitted Palladium by European eels (*Anguilla anguilla*) following experimental exposure to road dust. Environ Pollut 113:341–345

Sures B, Zimmermann S, Sonntag C (2003) The acanthocephalan *Paratenuisentis ambiguus* as a sensitive indicator of the precious metals Pt and Rh from automobile catalytic converters. Environ Pollut 122:401–405

Turner A, Lewis MS, Shams L, Brown MT (2007) Uptake of platinum group elements by the marine macroalga, *Ulva lactuca*. Mar Chem 105:271–280

Turner A, Pedroso SS, Brown MT (2008) Influence of salinity and humic substances on the uptake of trace metals by the marine macroalga, *Ulva lactuca*: Experimental observations and modelling using WHAM. Mar Chem 110:176–184

Vannini C, Domingo G, Marsoni M, Fumagalli A, Terzaghi R, Labra M, De Mattia F, Onelli E, Bracale M (2011) Physiological and molecular effects associated with palladium treatment in *Pseudokirchneriella subcapitata*. Aquat Toxicol 102:104–113

Veltz I, Arsac F, Biagianti-Risbourg S, Habets F, Lechenault H, Vernet G (1996) Effects of platinum (Pt4 +) on *Lubriculus variegatus* Müller (Annelida, Oligochaetae): acute toxicity and bioaccumulation. Arch Environ Contam Toxicol 31:63–67

Veltz I, Arsac F, Bouillot J, Collery P, Habets F, Lechenault H, Paicheler JC, Vernet G (1994) Ecotoxicological study of platinum using an experimental food chain. Preliminary results. In: Collery P, Poirier LA, Littlefield NA, Etienne JC (eds) Metal ions in biology and medicine. John Libbey Eurotext, Paris, pp 241–245

Ward JE, Shumway S (2004) Separating the grain from the chaff: particle selection in suspension- and deposit-feeding bivalves. J Exp Mar Biol Ecol 300:83–130

Zereini F, Alt F (2000) Anthropogenic platinum-group element emission: Their impact on man and environment. Springer, Berlin, Heidelberg, Germany

Zereini F, Alt F (2006) Palladium emissions in the environment: analytical methods, environmental assessment and health effects. Springer, Berlin, Heidelberg, Germany

Zimmermann S (2002) Untersuchungen zur Analytik und biologischen Verfügbarkeit der Platingruppenelemente Platin, Palladium und Rhodium. PhD thesis, University of Karlsruhe, Germany

Zimmermann S, Alt F, Messerschmidt J, von Bohlen A, Taraschewski H, Sures B (2002) Biological availability of traffic-related platinum-group elements (palladium, platinum, and rhodium) and other metals to the zebra mussel (*Dreissena polymorpha*) in water containing road dust. Environ Toxicol Chem 21:2713–2718

Zimmermann S, Baumann U, Taraschewski H, Sures B (2004) Accumulation and distribution of platinum and rhodium in the European eel *Anguilla anguilla* following aqueous exposure to metal salts. Environ Pollut 127:195–202

Zimmermann S, Messerschmidt J, von Bohlen A, Sures B (2005a) Uptake and bioaccumulation of platinum group metals (Pd, Pt, Rh) from automobile catalytic converter materials by the Zebra mussel (*Dreissena polymorpha*). Environ Res 98:203–209

Zimmermann S, Sures B (2004) Significance of platinum group metals from automobile exhaust gas converters for the biosphere. Environ Sci Pollut Res 11:194–199

Zimmermann S, von Bohlen A, Messerschmidt J, Sures B (2005b) Accumulation of the precious metals Platinum, Palladium and Rhodium from automobile catalytic converters in *Paratenuisentis ambiguus* (Eoacanthocephala) as compared with its fish host, *Anguilla anguilla*. J Helminthol 79:85–89

Biological Effects of PGE on Aquatic Organisms

Bernd Sures, Nadine Ruchter and Sonja Zimmermann

Abstract It is known since many years that the PGE Pt, Pd and Rh may have a range of negative effects on any forms of biota. Within this chapter the authors arrange literature data on these effects in the aquatic biosphere in a hierarchical model, which is used in ecotoxicology. This biomarker model helps to evaluate possible needs for further studies on specific levels. It emerges from the available data that a couple of adverse effects occurs if aquatic protists or organisms are exposed to PGE. However, usually relatively high exposure concentrations were applied exceeding current environmental concentrations of PGE. Moreover, most experiments focus on short exposure periods, which is in contrast to long lasting natural exposure conditions. Additionally, no information is available on effects of PGE on populations of organisms, as most studies are focussing on acute adverse effects of single test organisms. As a final conclusion it emerges that there is a strong need to perform multi-species studies addressing effects following exposure to chronic PGE concentrations as environmental concentrations of PGE still remain relatively low compared to effect concentrations of acute toxicity tests.

1 Indication of Adverse Effects Using Organisms

The well-being of organisms depends on many external and internal factors comprising a variety of abiotic and biotic conditions (Fig. 1). External conditions are usually summarized as the ecological niche of an organism. Most of the current textbook knowledge on the behaviour and physiology of organisms is collected in either laboratory based studies or under relatively pristine environmental conditions which are not always suitable to reflect real environmental conditions.

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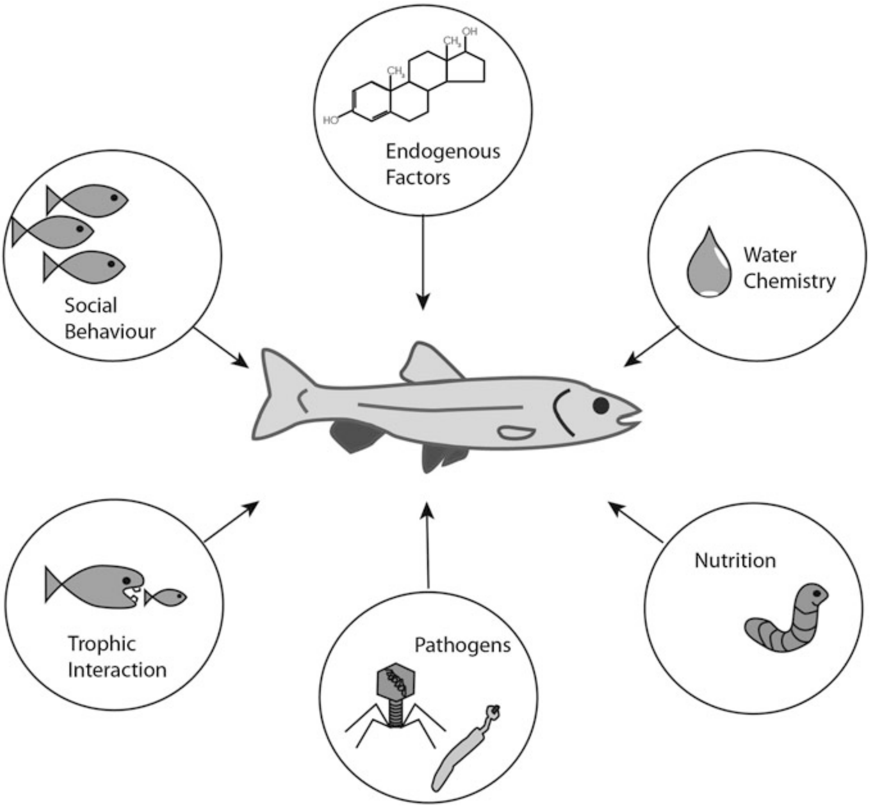

Fig. 1 Physiology and behaviour of organisms is affected by many internal and external parameters

Due to different environmental disasters mainly during the last century such as oil spills (e.g. Exxon Valdez, Prestige), accidents with nuclear power plants (Chernobyl) or the unintended introduction of toxic substances into food webs with severe effects on plants and animals including men (e.g. effects caused by DDT, PCBs, Itai-Itai, etc.) the formation of the discipline *ecotoxicology* was initiated (Fent 2013). This discipline causes an awareness of the fact that free living biota is threatened by environmental stressors such as pollutants which in turn may lead to severe changes in the organism's physiology and therefore have to be considered as one factor of the ecological niche. Accordingly, apart from understanding interactions of organisms with their environment under pristine conditions, knowledge on behaviour and physiology of organisms from polluted environments is important for both conservation strategies of the respective organisms as well as for prevention of toxicological effects in the ecosystem including all its abiotic and biotic components. This is a clear difference to the discipline *toxicology* which specifically concentrates on adverse effects of toxic substances on individual organisms with a clear focus on

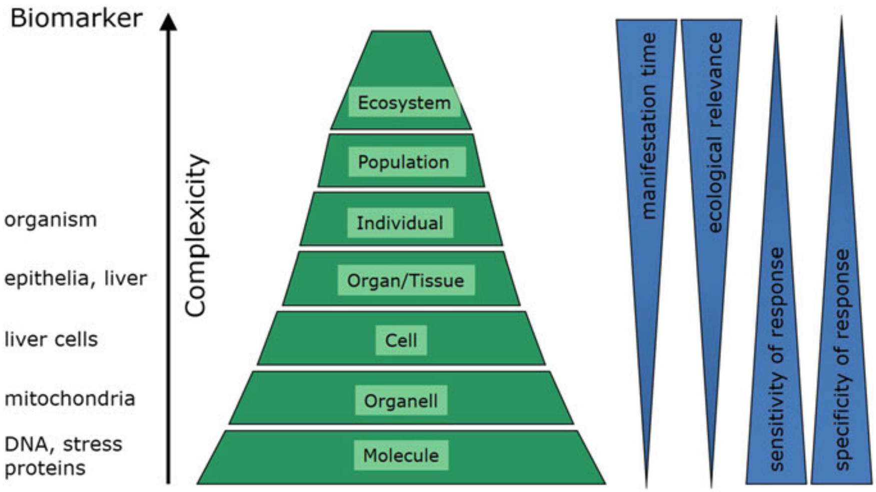

Fig. 2 The concept of biomarkers. Responses to environmental pollution lead to changes on different organisational levels. Examples for some of the markers are displayed on the *left side* of the diagram

humans (Gallo 2008). In ecotoxicology possible adverse effects of substances on ecosystems, their organisms and functions are investigated. Accordingly, sensitive and reliable tools are necessary to indicate the health status of organisms and ecosystems. Organisms used for accumulation of substances (accumulation bioindicators) enrich high amounts of certain substances inside their body (Amoozadeh et al. 2014). Chemical analyses of their tissues unravel the magnitude to which a substance of concern is stored in these organisms. As accumulated pollutants usually have adverse effects on the organism deviations from the normal physiological homeostasis will occur. If these changes are measurable, they can be used for effect indication and are called *biomarker*. Biomarker can be analysed on all levels of biological complexity (Fent 2013), ranging from the subcellular and molecular level to effects on populations or even whole ecosystems (Fig. 2).

The degree of environmental evidence is clearly correlated with the organisational level of the biomarker analysed. Changes in the expression level of a certain protein in an individual of an indicator species for example usually have no effects on the population or the ecosystem level. Similarly, these changes can be very pollutant-specific and occur immediately after exposure of the test organism. Differences concerning manifestation time, sensitivity and specificity of response as compared to the ecological relevance of a biomarker are summarized in Fig. 2.

To evaluate environmental risks of substances with unknown adverse effects on the environment it is advisable to investigate biomarkers from the very basal level upwards provided they can be taken up and accumulated by organisms. With respect to effects of the platinum group elements Pt, Pd and Rh laboratory exposure studies demonstrated considerable biological availability of PGE for different aquatic organisms such as plants (Farago and Parsons 1994; Veltz et al. 1994), mussels (Zimmermann et al. 2002), annelids (Veltz et al. 1996), crustaceans (Rauch and Morrison 1999; Sures and Radszuweit 2007) and fish (Jouhaud et al. 1999a, b; Sures et al. 2001).

In the following chapters some of the possible biological effects of Pt, Pd and Rh are summarized according to different biomarker levels mainly focussing on aquatic organisms.

2 Effects on the Molecular Level

There is a growing number of studies addressing detailed molecular interactions between platinum compounds and biological molecules in the context of human cancer treatment. The basics of this interaction are known for a long time (Hoppstock and Sures 2004) with a still ongoing development in order to optimizing cancer treatment. However, these studies are not considered here as they lack an environmental focus and belong to toxicological effects of PGE described in book Chap. "Mechanisms of Uptake and Interaction of Platinum Based Drugs in Eukaryotic Cells".

Molecular effects can be detected on DNA-, RNA- and protein-level, respectively. However, the total number of PGE studies on these levels is rather rare. Osterauer et al. (2011) investigated the genotoxicity of Pt for two freshwater organisms, the zebrafish (*Danio rerio*) and the ramshorn snail (*Marisa cornuarietis*) using exposure concentrations of 0, 0.1, 1, 10, 50, 100 and 200 μg/L $PtCl_2$ using the comet assay. No genotoxicity was found for *D. rerio* at the tested concentrations, whereas significantly elevated DNA damage was observed in *M. cornuarietis* at concentrations as low as 1 μg/L $PtCl_2$. These results suggest a high sensitivity of *M. cornuarietis* concerning the genotoxic impact of $PtCl_2$. As Ruchter (2012) could not detect genotoxic effects of Pt for *Corbicula* sp. when analysing the frequency of micronuclei in gill cells and hemocytes following Pt exposure there seems to be no general pattern of Pt gentoxicity to molluscs. Also Pd was shown to induce DNA changes in the genome of the freshwater algae *Pseudokirchneriella subcapitata*. Vannini et al. (2011) described significant levels of genomic modification using amplified fragment length polymorphism (AFLP) analysis following exposure of algae to 0.10 mg/L of K_2PdCl_4. Furthermore, significant decreases due to Pd exposure were confirmed at protein level using two dimensional gel electrophoresis and at mRNA level using semiquantitative RT-PCR for oxygen-evolving enhancer protein 2 as well as precursor and photosystem II stability/assembly factor HCF136 (Vannini et al. 2011). Accordingly, there is evidence that at least Pt and Pd do have genotoxic effects for the tested aquatic organisms.

To the best of our knowledge there is only a small number of papers concentrating on proteins as molecular markers in aquatic organisms. Singer et al. (2005) demonstrated that PGE can induce the production of heat shock proteins (hsp70) in the zebra mussel, *Dreissena polymorpha*, after exposure to soluble PGE standards for 10 weeks. Heat shock proteins allow organisms to expand their tolerance to a wider range of environmental stressors such as heat and pollutants, for example by acting as molecular chaperones, which bind to denatured and unfolded proteins, prevent aggregation of non-native proteins and repair damaged proteins (Werner and Hinton 1999; Tomanek and Sanford 2003). Under stressful conditions such as pollutant exposure an overexpression of heat shock proteins occurs, by which the stress tolerance can be enhanced (Feder and Hofmann 1999). These proteins were already used as biomarkers of adverse effects of other heavy metals, such as Pb and Cd (reviewed in Sanders 1993). In the study of Singer et al. (2005) the threshold levels for hsp70 induction decreased in the order: Cd > Pt > Pb ≥ Pd > Rh following exposure to metal salts with cation concentrations of 500 μg/L. The increase of hsp70 was time and metal dependent with elevated hsp70 levels between days 20 and 45 after beginning of the exposure. Highest hsp70 values were found for mussels exposed to Pd, followed by Pt and Rh. Values for hsp70 were 25-fold higher for Pd and 19-fold for Pt and Rh in comparison to control mussels. With a 6- and 12-fold increase of hsp70 due to Cd and Pb exposure, respectively, these well-known toxic metals showed a much lower effect than the PGE.

Also amphipods were tested for a possible induction of heat shock proteins due to exposure to Pd (Sures and Radszuweit 2007). Following a 24 days exposure to a nominal Pd concentration of 10 μg/L a 40-fold increase in the hsp70 concentration was described in *Gammarus roeseli*. This increase was only slightly lower than the hsp70 response following exposure of amphipods to heat which shows that Pd is recognized by amphipods as a harmful substance (Sures and Radszuweit 2007).

During embryonic development Osterauer et al. (2010a) investigated effects of $PtCl_2$ on the cellular and histological level using two different test organisms. Concentrations of hsp70 in the snail *M. cornuarietis* did not show any change following Pt exposure during early embryogenesis whereas hsp70 levels were significantly elevated at 100 μg/L $PtCl_2$ in larvae of the zebrafish *D. rerio*.

Metallothioneins as metal-specific biomarkers were analysed in *D. polymorpha* by Frank et al. (2008). Metallothioneins are proteins which are involved in maintenance of essential ions such as Zn (Coyle et al. 2002). In the context of ecotoxicology these proteins are part of detoxification processes of harmful metals such as Cd and Hg (Coyle et al. 2002). Accordingly, high levels of metallothioneins are used as biomarkers for metal pollution (Marie et al. 2006). Ten weeks exposure of *D. polymorpha* to different concentrations of Pd(II) resulted in a linear increase of metallothionein concentrations in the soft tissue of the mussels (Frank et al. 2008). Compared to initial metallothionein concentrations, an increase up to 600-, 160- and 27-fold after exposure to a Pd concentration of 500, 50 and 5 μg/L was found, respectively. These results demonstrate that also chronic exposure to low Pd concentrations causes effects on the molecular level. Induction of hsp and metallothioneins can also be analysed on a genetic level. Monetti et al. (2003) studied the expression of several genes, among them those encoding hsp70 and metallothioneins in 5 days old embryos and adults of *Xenopus laevis* exposed to Pt(II) and Pt(IV). Although no effect was found for hsp70- and metallothionein-genes in embryos and adults an overexpression of the type I collagen α-1 gene, which is known to be influenced by several metals was described (Monetti et al. 2003).

In summary, the studies on molecular effects mentioned above indicate general as well as metal-specific adverse effects of PGE on RNA-, DNA- and protein level at exposure concentrations in the low μg/L range for different aquatic organisms.

3 Effects on the Organelle Level

The most important organelles in cells are the nucleus, mitochondria and, with respect to plant cells, plastids. Again, only a few PGE studies focus on the organelle level, with even less papers considering aquatic species. Following Pd exposure of the freshwater unicellular green algae *Pseudokirchneriella subcapitata*, Vannini et al. (2011) found that the main cellular target for Pd is the chloroplast. Detailed analyses by transmission electron microscopy showed accumulation of precipitates, probably of Pd, in the chloroplasts. In numerous chloroplasts, some grana showed dilated thylakoids or isolated thylakoids that did not form grana. Additionally, some electron-opaque precipitates were visible in the chloroplast membranes. This preferential accumulation of Pd in the chloroplasts of *P. subcapitata* is correlated with a down-regulation of enzymes involved in carbon fixation. Accordingly, Pd-treated algae have a lowered capacity for CO_2 fixation and therefore only few chloroplasts with starch granules (Vannini et al. 2011).

In toxicity tests with $PtCl_2$ Osterauer et al. (2010a) observed vacuolisation of the cytoplasm in fish hepatocytes and irregular compartmentation of mucus cells of *Danio rerio* (details see below).

Although no study specifically dealing with effects of ionic PGE in mitochondria of aquatic protists is available, it is well known, that these organelles are sensitive to metal ions (Fent 2013) and are severely affected during cancer treatment using Pt compounds (Marullo et al. 2013). Exposure of yeast (*Saccharomyces cerevisia*) cells, however, suggested mitochondrial inhibition of aerobic respiration as a target effect (Frazzoli et al. 2007). Accordingly, it can be expected that if PGE ions enter the cell, they exhibit negative effects on mitochondria with subsequent problems concerning adenosine triphosphate (ATP) generation which is used as energy supply necessary to maintain cellular functions.

4 Effects on the Cellular Level

Cellular effects of substances are most often described using cell culture exposure experiments. Additional information on cellular effects derives from exposure studies of whole organisms in which microscopic techniques unravel cellular changes. Latter effects are described in the following chapter as they are the basis for effects on tissues and organs. Studies dealing with cellular effects were performed using human or prokaryotic cells whereas no cell cultures of aquatic animals like fish were tested so far. With respect to plants the aquatic unicellular green algae *Pseudokirchneriella subcapitata* appears to be the only aquatic species tested so far for PGE toxicity (Vannini et al. 2011, see above). Apart from the effects detected on the molecular and organelle level cellular degeneration was evident at K_2PdCl_4 concentrations of 500 µg/L (Vannini et al. 2011).

The effects of Pt, Pd and Rh as compared with Cd, Ni and Cr on cell viability and oxidative stress response using soluble metal salts were studied in the human bronchial epithelial cell line BEAS-2B (Schmid et al. 2007). These exposure experiments demonstrate that Rh(III) showed little influence whereas Pt(II), Pt(IV) and Pd(II), respectively, had significant effects on cell viability at levels comparable to Cd(II) and Cr(VI). An induction of reactive oxygen species (ROS) was also found in these cells with a maximum relative increase in ROS production for Pt(IV) of 1,134 % that was more than twice as high as for Cr(VI) (560 %) and for Pt(II) (238 %).

By using *Photobacterium phosphoreum* within the standardized Microtox Test EC_{50}—values were found to decrease in the following manner: $Pt > Pd = Rh$ (Rauch 2001).

Metal toxicity, measured by inhibition of normalized oxygen uptakes in *Saccharomyces cerevisia* increased significantly with the dose and thus the PGE accumulation in the yeast cells (Frazzoli et al. 2007). In contrast to the studies cited above, however, Rh was found to be generally more toxic to yeast cells than Pd and Pt with EC_{10} values of 51, 85 and 187 ng/g for Rh, Pd and Pt, respectively, (Frazzoli et al. 2007).

Taken together, these findings underline the strong effects PGE can have on cell metabolism and emphasize the need for further mechanistic studies of their toxic properties.

5 Effects on the Level of Tissues/Organs

Similar to effects on organelles, which are mentioned in studies on cellular effects, adverse effects on organs or tissues of plants and animals are usually part of investigations dealing with individual organisms. However, possible histopathological alterations during early embryogenesis in the zebrafish, *Danio rerio* and the ramshorn snail, *Marisa cornuarietis* were specifically addressed in a study by Osterauer et al. (2010a). At the early stage of development clear histopathological effects in *D. rerio* were found for liver and gut tissue. In fish liver inflammatory reactions with increasing numbers of macrophages, dilation of capillary spaces and high variability in the density of cytoplasm and/or nuclei, occurred following exposure to 1 µg/L of $PtCl_2$ (and higher). Further prominent effects especially at the highest concentrations of 50 and 100 µg/L $PtCl_2$ were vacuolisation of the cytoplasm, beginning of cloudy swelling of the hepatocytes, and caryopycnosis. Concerning fish gut the most dominant effects of Pt were ablation of gut cells from the basal lamina, basal vacuolisation of the cytoplasm, irregular compartmentation, and an increase in the number of mucus cells. These effects were prominent from 1 µg/L $PtCl_2$ onwards, getting more severe at higher concentrations.

In the ramshorn snail histopathological investigations revealed effects of Pt on epidermis, hepatopancreas, and gills. Whereas only little modification of the epidermal structure occurred due to Pt exposure, the hepatopancreas, as an organ for storage and detoxification of heavy metals, as well as the gills, which have been permanently in direct contact with the metal, were modified and showed strong reactions due to Pt exposure.

These results demonstrate that Pt is capable of inducing histopathological alterations in the tissues of the freshwater organisms *D. rerio* and *M. cornuarietis* during early embryogenesis. As effects during this critical period of development are not routinely investigated, the results of Osterauer et al. (2010a) clearly claim for more studies addressing this issue.

Also adult fish tissues are negatively affected following exposure to Pt (Jouhaud et al. 1999a, b). Degenerative effects such as lysis and necrosis of mucosal cells as well as changes in submucosa structure and adaptative fusion between villi were described for intestinal tissues. The extent and severity of these gut alterations were time- and concentration-dependent.

6 Effects on the Level of Individual Organisms

For most of the studies mentioned above biological effects of PGE on aquatic individuals were investigated using soluble PGE species in exposure and toxicity studies. The range of organisms tested so far comprises five plant species and different taxa of animals including acanthocephalans (parasites), gastropods and bivalves (molluscs), annelids (worms), crustaceans, and two taxa of vertebrates i.e. fish and amphibians (see Table 1). The most commonly analysed effect on the level of organisms is the bioaccumulation of PGE. It emerges that depending on the water characteristics usually Pd shows the highest uptake rates followed by Pt, whereas Rh accumulation is always least (Zimmermann and Sures 2004; further details in book Chap. "Laboratory Studies on the Uptake and Bioaccumulation of PGE by Aquatic Plants and Animals" by Zimmermann et al. (2014)). Bioaccumulation is a fundamental step as the degree of metal accumulation determines the severity of adverse effects the metal has on the organism. Next to bioaccumulation studies many acute toxicity tests were performed with different taxa in order to determine the medium lethal concentration at which 50 % of the test individuals died (LC_{50}). These studies reveal that Pt appears to be the most toxic element of the three PGE (e.g. Borgmann et al. 2005). Toxicity of Pt, however, was far behind the toxicity of e.g. Cd, Cr, Hg and Pb, and it was assumed to be as toxic as Se, Ce and Lu (Borgmann et al. 2005). Besides acute toxicity tests also sublethal effects were studied. Most of them focus on either non-lethal effects of PGE exposure on adult test species by determining effect concentrations (EC_{50}) or investigate the interaction between PGE exposure and embryonic development. Concerning the group

Table 1 Aquatic test organisms used for laboratory studies on biological effects

	Species	PGE	Investigated effect	Reference
Plants	*Eichhornia crassipes*	Pt, Pd, Rh (Ru, Ir, Os)	Bioaccumulation, amino acid composition	Farago and Parsons (1994)
	Lemna minor	Pt	Bioaccumulation, growth, leaf colour	Veltz et al. (1994)
	Fontinalis antipyretica	Pt	Bioaccumulation	Veltz et al. (1994)
	Elodea canadensis	Pt, Pd, Rh	Bioaccumulation, chlorophyll content	Diehl and Gagnon (2007)
	Ulva lactuca	Pt, Pd, Rh	Bioaccumulation	Turner et al. (2007, 2008), Masakorala et al. (2008)
	Ulva lactuca	Pt	Bioaccumulation, photochemical energy conversion	Easton et al. (2011)
	Pseudokirchneriella subcapitata	Pd	Bioaccumulation, growth, morphology, photosynthetic pigment composition, proteomic and DNA changes	Vannini et al. (2011)
Acanthocephala	*Pomphorhynchus laevis*	Pt, Pd, Rh	Bioaccumulation	Sures et al. (2005), Ruchter (2012)
	Pomphorhynchus tereticollis	Pt	Bioaccumulation	Ruchter (2012)
	Paratenuisentis ambiguus	Pt, Pd, Rh	Bioaccumulation	Sures et al. (2003), Zimmermann et al. (2005a)
	Polymorphus minutus	Pd	Bioaccumulation, heat shock proteins (Hsp70)	Sures and Radszuweit (2007)

(continued)

Table 1 (continued)

	Species	PGE	Investigated effect	Reference
Molluscs	*Littorina littorea*	Pt, Pd, Rh	Bioaccumulation	Mulholland and Turner (2011)
	Marisa cornuarietis	Pt, Pd	Embryonic development	Sawasdee and Köhler (2009), Osterauer et al. (2010b)
	Marisa cornuarietis	Pt	Bioaccumulation, heart rate, hatching rate, histopathological alterations, heat shock proteins, genotoxicity	Osterauer et al. (2009, 2010a, 2011)
	Corbicula sp.	Pt	Bioaccumulation, genotoxicity	Ruchter (2012)
	Dreissena polymorpha	Pt, Pd, Rh	Bioaccumulation, heat shock proteins (HSP70), metallothioneins	Zimmermann et al. (2002, 2005b), Singer et al. (2005), Sures and Zimmermann (2007), Frank et al. (2008)
Annelida	*Lumbriculus variegatus*	Pt	Bioaccumulation, lethality (e.g. LC_{50}), body degeneration, epidermal effect, cephalic regeneration	Veltz et al. (1994, 1996), Veltz-Balatre et al. (2000)
	Tubifex tubifex	Pt, Pd	Immobilization (EC_{50})	Khangarot (1991)
	Arenicola marina	Pt, Pd	Bioaccumulation	French and Turner (2008)
Crustacea	*Daphnia magna*	Pt	Lethality (LC_{50}), reproductive impairment, body weight, total protein, aspartate transaminase activity (GOT: glutamic oxalacetic transaminase)	Biesinger and Christensen (1972)
	Cypris subglobosa	Pt, Pd	immobilization (EC_{50})	Khangarot and Das (2009)
	Asellus aquaticus	Pt, Pd, Rh	Bioaccumulation	Rauch and Morrison (1999), Moldovan et al. (2001)
	Hyallela azteca	Pt, Pd, Rh (Ru, Ir, Os)	Bioaccumulation, lethality (LC_{50})	Borgmann et al. (2005)
	Gammarus roeseli	Pd	Bioaccumulation, heat shock proteins (Hsp70)	Sures and Radszuweit (2007)

(continued)

Table 1 (continued)

	Species	PGE	Investigated effect	Reference
Fish	*Lebistes reticulates*	Pt	Acute toxicity to juveniles	Veltz et al. (1994)
	Oncorhynchus kisutch	Pt	Opercular movement, hypoactivity, growth, histopathological alterations	Ferreira and Wolke (1979)
	Danio rerio	Pt	Bioaccumulation, intestinal histopathological alterations	Jouhaud et al. (1999a, b)
	Danio rerio	Pt	Bioaccumulation, heart rate, hatching rate, histopathological alterations, heat shock proteins, genotoxicity	Osterauer et al. (2009, 2010a, 2011)
	Anguilla anguilla	Pt, Pd, Rh	Bioaccumulation	Sures et al. (2001, 2003), Zimmermann et al. (2004, 2005a)
	Squalius cephalus	Pt	Bioaccumulation, genotoxicity	Ruchter (2012)
	Barbus barbus	Pt, Pd, Rh	Bioaccumulation	Sures et al. (2005)
Amphibia	*Xenopus laevis*	Pt	Bioaccumulation, embryotoxicity, teratogenicity, gene expression (e.g. hsp70, metallothionein)	Monetti et al. (2003)

of latter test procedures one of the most remarkable results is the prevention of external shell formation in the prosobranch gastropod *Marisa cornuarietis* following short-term exposure to platinum during embryonic development (Osterauer et al. 2010b). Further effects for which EC_{50} values were determined comprise reduction of weight and enzyme activity alterations (Table 1). All exposure studies summarized here, were conducted with PGE concentrations far above environmental levels. Therefore, it is unlikely to find acute or sublethal PGE-induced toxicity under field conditions for aquatic organisms. Unfortunately, only little information is available on chronic effects of aquatic organisms exposed to environmental PGE concentrations (Haus et al. 2010, see also book Chap. "Field Studies on PGE in AquaticEcosystems" by Ruchter et al. (2014)).

7 Effects on the Population Level

A common approach to evaluate adverse effects for populations would be to analyse the genetic diversity of populations under pollution stress (Nowak et al. 2009, 2012). To the best of our knowledge no such study is available addressing PGE. However, as different genotoxic as well as cytotoxic effects were described so far, there is an urgent need to evaluate potential negative effects of PGE on population structure. Especially for gastropods it seems to be advisable to perform more generation exposure studies as negative effects on shell formation may also manifest on the population level of the respective gastropod population.

8 Effects on the Ecosystem Level

Ecosystems represent the highest level of biological organization comprising populations of all occurring species as well as their interaction with the abiotic environment. As information of negative effects on whole ecosystems is usually missing the only available proxy is to refer to results from microcosm studies. Microcosms are simplified artificial ecosystems containing members of different trophic levels (Walker et al. 2012). They are used to simulate and predict the behaviour of toxic substances in natural ecosystems under controlled laboratory conditions. Compared to single species studies complex interaction between organisms (see also Fig. 1) as well as biomagnification processes are considered in microcosms. Due to the complexity of performing microcosm experiments only two papers have been published with respect to PGE. Rauch et al. (2004) investigated the influence of Pt on the photosynthetic activity of a natural grown periphyton community. As no other organisms belonging to different trophic levels were investigated this investigations cannot be considered a real microcosm study, however as different populations were similarly investigated it clearly range above the population level. No significant difference could be found for periphyton communities exposed in river water to Pt in comparison to the control group. Interestingly, the photosynthetic activity decreased only in the periphyton community in the reference water.

French and Turner (2008) used natural marine sediments, water and the polychaete *Arenicola marina* as test system in which they introduced Pt and Pd as either soluble standards or in particulate form. This design again represents a very basal microcosm as biological interactions between species cannot be considered using a one-species design. Emphasis during this investigation was on bioaccumulation of the metals in the polychaetes. Additionally, partitioning of PGE at the sediment–water interface and bioturbation were analysed in microcosms with and without *A. marina* to unravel the relevance of biota for metal concentrations in sediments and the water column. It turned out that *A. marina* represents an important vehicle for the subduction and cycling of catalytic converter particles. The polychaetes themselves accumulate Pt and Pd and cause the (re)mobilization and adsorption of both metals that are either associated with particles or that enter the environment in a soluble form.

Both microcosm studies indicate that biota may have effects on the partitioning of PGE between abiotic matrices and that biota may be affected by these metals in the sense that bioaccumulation occurs. Additional adverse effects of PGE on ecosystems could not be described so far. Apart from the fact that environmental PGE concentrations still remain relatively low, the diversity of stressors similarly occurring in ecosystems impede to separating effects of PGE and those of other pollutants or parameters as shown in Fig. 1.

In a broader sense many of the field studies published so far on PGE in abiotic and biotic matrices (see also book Chap. "Field Studies on PGE in Aquatic Ecosystems" by Ruchter et al. (2014)) can be considered as studies addressing the ecosystem level. However, even if different taxa were studied (see e.g. Haus et al. 2007) they do not belong to different trophic levels within one food chain. Accordingly, to really evaluate effects of PGE on the ecosystem level, appropriate studies are still missing. Similarly, they are justified due to the occurrence of relevant effects on lower biomarker levels (molecular, individuals).

9 Conclusion

The studies summarized within this chapter show that a couple of adverse effects occur if aquatic protists or organisms are exposed to PGE. However, usually relatively high concentrations were necessary in order to induce significant effects on one of the biomarkers levels. The effective concentrations applied so far clearly exceed current environmental concentrations of PGE. Moreover experiments are usually performed with short exposure periods, which is not a realistic approach to match natural conditions. In the environment pollutant exposure may last for month or even years. With respect to the rather low environmental PGE concentrations there is a clear need for studies using chronic PGE concentrations and which are addressing the genetic diversity of populations under PGE pollution stress. However, as there are also severe alterations such as the prevention of external shell formation in snails, we have to make sure that PGE levels in the environment will not increase to critical levels. In order to reach this goal a thorough monitoring of PGE levels in abiotic and biotic matrices in the environment is the most important first step that has to be implemented at least for highly polluted sites such as sewage canals and urban stormwater retention ponds.

References

Amoozadeh E, Malek M, Rashidinejad R, Nabavi SM, Karbassi MR, Ghayoumi R, Ghorbanzadeh-Zafarni G, Salehi H, Sures B (2014) Marine organisms as heavy metal bioindicators in the Persian Gulf and the Gulf of Oman. Environ Sci Pollut Res 21:2386–2395

Biesinger KE, Christensen GM (1972) Effects of various metals on survival, growth, reproduction, and metabolism of *Daphnia magna*. J Fish Res Board Canada 29:1691–1700

Borgmann U, Couillard Y, Doyle P, Dixon DG (2005) Toxicity of sixty-three metals and metalloids to *Hyalella azteca* at two levels of water hardness. Environ Toxicol Chem 24:641–652

Coyle P, Philcox J, Carey L, Rofe A (2002) Metallothionein: the multipurpose protein. Cell Mol Life 59:627–647

Diehl DB, Gagnon ZE (2007) Interactions between essential nutrients with platinum group metals in submerged aquatic and emergent plants. Water Air Soil Pollut 184:255–267

Easton C, Turner A, Sewell G (2011) An evaluation of the toxicity and bioaccumulation of cisplatin in the marine environment using the macroalga, *Ulva lactuca*. Environ Pollut 159:3504–3508

Farago ME, Parsons PJ (1994) The effects of various platinum metal species on the water plant *Eichhornia crassipes* (MART.) Solms. Chem Speciat Bioavailab 6:1–12

Feder M, Hofmann GE (1999) Heat-shock proteins, molecular chaperones, and the stress response: evolutionary and ecological physiology. Ann Rev Physiol 61:243–282

Fent K (2013) Ökotoxikologie: Umweltchemie, Toxikologie. Ökologie, Thieme Verlag

Ferreira PF, Wolke RE (1979) Acute toxicity of platinum to Coho salmon (*Oncorhynchus kisutch*). Mar Poll Bull 10:79–83

Frank SN, Singer C, Sures B (2008) Metallothionein (MT) response after chronic palladium exposure in the zebra mussel, *Dreissena polymorpha*. Environ Res 108:309–314

Frazzoli C, Dragone R, Mantovani A, Massimi C, Campanella L (2007) Functional toxicity and tolerance patterns of bioavailable Pd(II), Pt(II), and Rh(III) on suspended *Saccharomyces cerevisiae* cells assayed in tandem by a respirometric biosensor. Anal Bioanal Chem 389:2185–2194

French B, Turner A (2008) Mobilization, adsorption, and bioavailability of Pt and Pd in coastal sediments: the role of the polychaete, *Arenicola marina*. Environ Sci Technol 42:3543–3549

Gallo MA (2008) History and scope of toxicology. In: Shanahan F, Naglieri C (eds) Cassarett and doul's toxicology: the basic science of poison, 7th edn. The McGraw-Hill Companies, New York, pp 3–10

Haus N, Zimmermann S, Sures B (2010) Precious metals in urban aquatic systems: platinum, palladium and rhodium: sources, occurrence, bioavailability and effects. In: Fatta-Kasinos D, Bester K, Kümmerer K (eds) Xenobiotics in the urban water cycle: mass flows, environmental processes, mitigation and treatment strategies. Springer, The Netherlands, pp 73–86

Haus DN, Zimmermann S, Wiegand J, Sures B (2007) Occurrence of platinum and additional traffic related heavy metals in sediments and biota. Chemosphere 66:619–629

Hoppstock K, Sures B (2004) Platinum group metals. In: Merian E, Anke M, Ihnat M, Stoeppler M (eds) Elements and their compounds in the environment. Wiley-VCH, Weinheim, pp 1047–1086

Jouhaud R, Biagianti-Risbourg S, Vernet G (1999a) Atteintes ultrastructurales intestinales induites par une concentration subléthale de platine chez le téléostéen Brachydanio rerio. Bulletin de la Société zoologique de France 124:111–116

Jouhaud R, Biagianti-Risbourg S, Vernet G (1999b) Effets du platine chez *Brachydanio rerio* (Téléostéen, Cyprinidé). I. Toxicité aiguë; bioaccumulation et histopathologie intestinales. J Appl Ichthyol 15:41–48

Khangarot BS (1991) Toxicity of metals to a freshwater tubificid worm, *Tubifex tubifex* (Müller). Bull Environ Contam Toxicol 46:906–912

Khangarot BS, Das S (2009) Acute toxicity of metals and reference toxicants to a freshwater ostracod, *Cypris subglobosa* Sowerby, 1840 and correlation to EC_{50} values of other test models. J Hazard Mat 172:641–649

Marie V, Baudrimont M, Boudou A (2006) Cadmium and zinc bioaccumulation and metallothionein response in two freshwater bivalves (*Corbicula fluminea* and *Dreissena polymorpha*) transplanted along a polymetallic gradient. Chemosphere 65:609–617

Marullo R, Werner E, Degtyareva N, Moore B, Altavilla G, Ramalingam SS, Doetsch PW (2013) Cisplatin induces a mitochondrial-ROS response that contributes to cytotoxicity depending on mitochondrial redox status and bioenergetic functions. PLoS One 8:e81162

Masakorala K, Turner A, Brown MT (2008) Influence of synthetic surfactants on the uptake of Pd, Cd and Pb by the marine macroalga, *Ulva lactuca*. Environ Pollut 156:897–904

Moldovan M, Rauch S, Gomez M, Palacios MA, Morrison GM (2001) Bioaccumulation of palladium, platinum and rhodium from urban particulates and sediments by the freshwater isopod *Asellus aquaticus*. Water Res 35:4175–4183

Monetti C, Bernardini G, Vigetti D, Prati M, Fortaner S, Sabbioni E, Gornati R (2003) Platinum toxicity and gene expression in *Xenopus embryos*: Analysis by FETAX and differential display. Altern Lab Anim 31:401–408

Mulholland R, Turner A (2011) Accumulation of platinum group elements by the marine gastropod *Littorina littorea*. Environ Pollut 159:977–982

Nejdl L,, Kudr J, Blazkova I, Chudobova D, Skalickova S, Ruttkay-Nedecky B, Adam V, Kizek R (2014) The mechanism of platinum metals action on eukaryotic cell and their potential risks to humans, animals and environment

Nowak C, Vogt C, Oehlmann J, Pfenninger M, Schwenk K, Streit B, Oetken M (2012) Impact of genetic diversity and inbreeding on the life-history of *Chironomus* midges over consecutive generations. Chemosphere 88:988–993

Nowak C, Vogt C, Pfenninger M, Schwenk K, Oehlmann J, Streit B, Oetken M (2009) Rapid genetic erosion in pollutant-exposed experimental chironomid populations. Environ Pollut 157:881–886

Osterauer R, Faßbender C, Braunbeck T, Köhler HR (2011) Genotoxicity of platinum in embryos of zebrafish (*Danio rerio*) and ramshorn snail (*Marisa cornuarietis*). Sci Total Environ 409:2114–2119

Osterauer R, Haus N, Sures B, Köhler HR (2009) Uptake of platinum by zebrafish (*Danio rerio*) and ramshorn snail (*Marisa cornuarietis*) and resulting effects on early embryogenesis. Chemosphere 77:975–982

Osterauer R, Köhler HR, Triebskorn R (2010a) Histopathological alterations and induction of hsp70 in ramshorn snail (*Marisa cornuarietis*) and zebrafish (*Danio rerio*) embryos after exposure to $PtCl_2$. Aquatic Toxicol 99:100–107

Osterauer R, Marschner L, Betz O, Gerberding M, Sawasdee B, Cloetens P, Sures B, Triebskorn R, Köhler HR (2010b) Turning snails into slugs: induced body plan changes and formation of an internal shell. Evolut Dev 12:474–483

Rauch S (2001) On the environmental relevance of platinum group elements. PhD thesis, Chalmers University of Technology, Göteborg, Sweden

Rauch S, Morrison GM (1999) Platinum uptake by the freshwater isopod *Asellus aquaticus* in urban rivers. Sci Total Environ 235:261–268

Rauch S, Paulsson M, Wilewska M, Blanck H, Morrison GM (2004) Short-term toxicity and binding of platinum to freshwater periphyton communities. Arch Environ Contam Toxicol 47:290–296

Ruchter N (2012) Ecotoxicology of traffic related Platinum in the freshwater environment. PhD thesis, University of Duisburg-Essen

Ruchter N, Zimmermann S, Sures B (2014) Field studies on PGE in aquatic biota. In: Zereini F, Wiseman CLS (eds) Platinum Metals in the Environment. Springer. doi:10.1007/978-3-662-44559-4_22

Sanders B (1993) Stress proteins in aquatic organisms: an environmental perspective. Crit Rev Toxicol 23:49–75

Sawasdee B, Köhler HR (2009) Embryo toxicity of pesticides and heavy metals to the ramshorn snail, *Marisa cornuarietis* (Prosobranchia). Chemosphere 75:1539–1547

Schmid M, Zimmermann S, Krug HF, Sures B (2007) Influence of platinum, palladium and rhodium as compared with cadmium, nickel and chromium on cell vitality and oxidative stress in human bronchial epithelial cells. Environ Int 33:385–390

Singer C, Zimmermann S, Sures B (2005) Induction of heat shock proteins (hsp70) in the zebra mussel (*Dreissena polymorpha*) following exposure to platinum group metals (platinum, palladium and rhodium): Comparison with lead and cadmium exposures. Aquatic Toxicol 75:65–75

Sures B, Radszuweit H (2007) Pollution induced heat shock protein expression in the amphipod *Gammarus roeseli* is affected by larvae of *Polymorphus minutus* (Acanthocephala). J Helminthol 81:191–197

Sures B, Thielen F, Baska F, Messerschmidt J, von Bohlen A (2005) The intestinal parasite *Pomphorhynchus laevis* as a sensitive accumulation indicator for the platinum group metals Pt, Pd and Rh. Environ Res 98:83–88

Sures B, Zimmermann S (2007) Impact of humic substances on the aqueous solubility, uptake and bioaccumulation of platinum, palladium and rhodium in exposure studies with *Dreissena polymorpha*. Environ Pollut 146:444–451

Sures B, Zimmermann S, Messerschmidt J, von Bohlen A, Alt F (2001) First report on the uptake of automobile catalyst emitted palladium by European eels (*Anguilla anguilla*) following experimental exposure to road dust. Environ Pollut 113:341–345

Sures B, Zimmermann S, Sonntag C, Stüben D, Taraschewski H (2003) The acanthocephalan *Paratenuisentis ambiguus* as a sensitive indicator of the precious metals Pt and Rh emitted from automobile catalytic converters. Environ Pollut 122:401–405

Tomanek L, Sanford E (2003) Heat-shock protein 70 (Hsp70) as a biochemical stress indicator: an experimental field test in two congeneric intertidal gastropods (Genus: *Tegula*). Biol Bull 205:276–284

Turner A, Lewis MS, Shams L, Brown MT (2007) Uptake of platinum group elements by the marine macroalga, *Ulva lactuca*. Mar Chem 105:271–280

Turner A, Pedroso SS, Brown MT (2008) Influence of salinity and humic substances on the uptake of trace metals by the marine macroalga, *Ulva lactuca*: Experimental observations and modelling using WHAM. Mar Chem 110:176–184

Vannini C, Domingo G, Marsoni M, Fumagalli A, Terzaghi R, Labra M, De Mattia F, Onelli E, Bracale M (2011) Physiological and molecular effects associated with palladium treatment in *Pseudokirchneriella subcapitata*. Aquatic Toxicol 102:104–113

Veltz I, Arsac F, Biagianti-Risbourg S, Habets F, Lechenault H, Vernet G (1996) Effects of platinum (Pt^{4+}) on *Lumbriculus variegatus* Müller (Annelida, Oligochaetae): Acute toxicity and bioaccumulation. Arch Environ Contam Toxicol 31:63–67

Veltz I, Arsac F, Bouillot J, Collery P, Habets F, Lechenault H, Paicheler JC, Vernet G (1994) Ecotoxicological study of platinum using an experimental food chain. Preliminary results. In: Collery P, Poirier LA, Littlefield NA, Etienne JC, (eds) Metal ions in biology and medicine. John Libbey Eurotext, Paris, pp 241–245

Veltz-Balatre I, Biagianti-Risbourg S, Vernet G (2000) De la régénération céphalique de l'ologochète Lumbriculus variegatus Müller à l'étude de la toxicité des métaux lourds. Année Biol 39:39–52

Walker CH, Sibly RM, Hopkin SP, Peakall DB (2012) Principles of ecotoxicology, 4th edn. CRC Press, Boca Raton

Werner I, Hinton DE (1999) Spatial profiles of hsp70 proteins in Asian clam (*Potamocorbula amurensis*) in northern San Francisco Bay may be linked to natural rather than anthropogenic stressors. Mar Environ Res 50:379–384

Zimmermann S, Sures B (2004) Significance of platinum group metals emitted from automobile exhaust gas converters for the biosphere. Environ Sci Pollut Res 11:194–199

Zimmermann S, Alt F, Messerschmidt J, von Bohlen A, Taraschewski H, Sures B (2002) Biological availability of traffic related platinum group elements (palladium, platinum, and rhodium) and other metals to the zebra mussel (*Dreissena polymorpha*) in water containing road dust. Environ Toxicol Chem 21:2713–2718

Zimmermann S, Baumann U, Taraschewski H, Sures B (2004) Accumulation and distribution of platinum and rhodium in the European eel *Anguilla anguilla* following aqueous exposure to metal salts. Environ Pollut 127:195–202

Zimmermann S, Messerschmidt J, von Bohlen A, Sures B (2005a) Accumulation of the precious metals platinum, palladium and rhodium from automobile catalytic converters in *Paratenuisentis ambiguus* as compared with its fish host, *Anguilla anguilla*. J Helminthol 79:85–89

Zimmermann S, Messerschmidt J, von Bohlen A, Sures B (2005b) Uptake and bioaccumulation of platinum group metals (Pd, Pt, Rh) from automobile catalyst converter materials by the Zebra mussel (*Dreissena polymorpha*). Environ Res 98:203–209

Zimmermann S, Sures B, Ruchter N (2014) Laboratory studies on the uptake and bioaccumulation of PGE by plants and animals. In: Zereini F, Wiseman CLS (eds) Platinum Metals in the Environment. Springer. doi:10.1007/978-3-662-44559-4_23

Mechanisms of Uptake and Interaction of Platinum Based Drugs in Eukaryotic Cells

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Abstract The platinum group elements are significant compounds used in numerous fields of human life. Besides of often discussed toxic effect the platinum compounds show the therapeutic effects. Nowadays, platinum-based cytostatic are still the most frequently used drugs in oncology. Due to their proved medicinal purposes the behavior in the organism should to be intensively studied as well as their interactions with DNA and other important biological molecules. This review summarizes the recent results in the platinum drug field and discusses the behavior of platinum compounds in cells. The interaction of platinum and DNA with respect to the change of the DNA structure are also clarified.

1 Introduction

Platinum group elements (PGEs) can be naturally found only at very low concentration (Sikorova et al. 2011). They are emitted to the environment predominantly in the metallic form, and therefore have been considered to be inert and their bioavailability to be low. PGEs contamination occurs in airborne particulate matter (Zereini et al. 2005), roadside dust (Gomez et al. 2002), soil (Zereini et al. 2007), vegetation (Hooda et al. 2008) and water, which finally results in bioaccumulation of these elements in the living organisms (Ravindra et al. 2004). Emissions of platinum metals and grow of their concentrations in the environment lead to the questions about their potential to have a negative effect on the human health

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(Sikorova et al. 2011). Platinum compounds exhibiting toxic, carcinogenic or mutagenic effects (Wang and Li 2012).

Platinum due to its physicochemical properties is used in many sectors. Its ability to catalyze various chemical reactions is used in automotive industry, organic and inorganic chemistry and designing of sensors and biosensors (Siriviriyanun et al. 2013; Yang et al. 2013; Eremia et al. 2013). Exhaust gases from combustion engines are purified by platinum-based catalytic converters (Piskulov and Chiu 2013) and can be improved by synergic effect of platinum and Bronsted acid (Fu et al. 2013). The platinum plays an important role in hydrogenation, oxidation, dehydrogenation, hydrogenolysis (Furstner 2009) and is used in synthesis of acetic acid (carbonylation), n-butanal (hydroformylation) (Crundwell et al. 2011), polymers (Ikeda et al. 2000) etc.

Platinum compounds are still the most effective cytostatic drugs, although Ru (II), Os(II), Ir(II) etc. have a quite similar properties (Dhahagani et al. 2014). New generations of platinum (complexes and nanoparticles) chemotherapeutics offer the prospect of combating platinum resistance and expanding the range of treatable cancers. The best known platinum cytostatic drugs are shown in Fig. 1.

Nanotransporters (micelles, dendrimers, liposomes, nanoparticles) (Oberoi et al. 2013; Gheybi et al. 2014) and platinum-peptide complexes are used to overcome this side effects (Graf et al. 2012). Recently it was revealed that metal nanoparticles can have similar anti-tumor effect as platinum complexes and its anti-tumor properties mostly depend on a size and material (Manikandan et al. 2013). However, as it is shown in Fig. 2, platinum related research is still far more related to medicine (Ali et al. 2013; Muscella et al. 2013; Ruggiero et al. 2013).

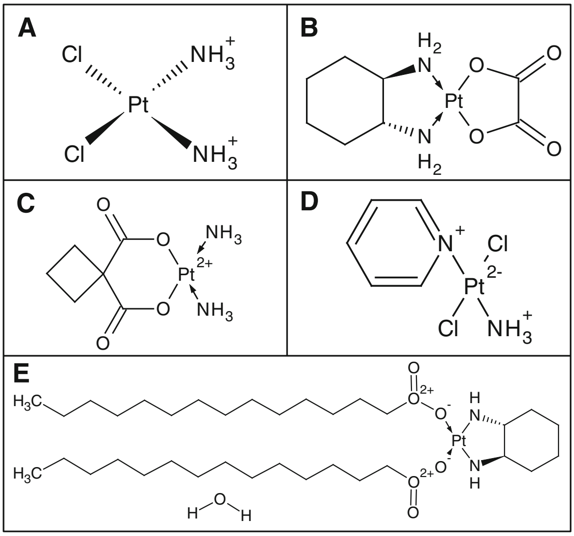

Fig. 1 The table of different Pt-drugs mentioned in the text and their chemical structures: *A* Cisplatin, *B* Carboplatin, *C* Oxaliplatin, *D* Miriplatin, *E* Ampyplatin

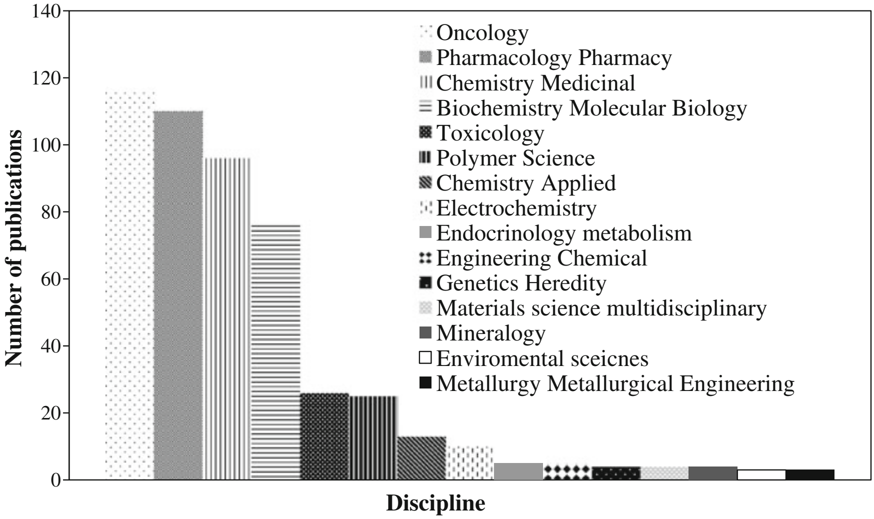

Fig. 2 The analyzed results from Web of Science database with the keyword “platinum”

2 The Effects of Platinum Compounds on Eukaryotic Cells and Their Interaction with DNA

Metals are ubiquitous and essential for cellular processes in all living organisms and theirs availability determined the life on the Earth (Gitlin and Lill 2006; Florea and Büsselberg 2011). The cell biology of metals is residing at the interface of chemistry, biology, pharmacology and medicine (Gitlin and Lill 2012; Sawyer 2006). Their special properties including redox activity, variable coordination modes and reactivity towards organic substrates are the reasons, why all transition metals are potentially toxic for cells and their intracellular concentration is tightly regulated by uptake, storage and secretion. Although the importance of metals in biology have been recognized, knowledge about metals trafficking and metabolism is still limited (Gitlin and Lill 2006).

2.1 Cellular Uptake Mechanisms of the Platinum Complexes

The effects of platinum complexes on a cell are studied mainly because platinum compounds play over 40 years a central role in cancer chemotherapy (Galanski et al. 2005). Although cisplatin is an important cytotoxic agent in the treatment of epithelial malignancies, it has several disadvantages. It damages, indiscriminately, cancerous and normal tissues. The main adverse effects of cisplatin includes renal toxicity, gastrointestinal toxicity, peripheral neuropathy, myelotoxicity, asthenia,

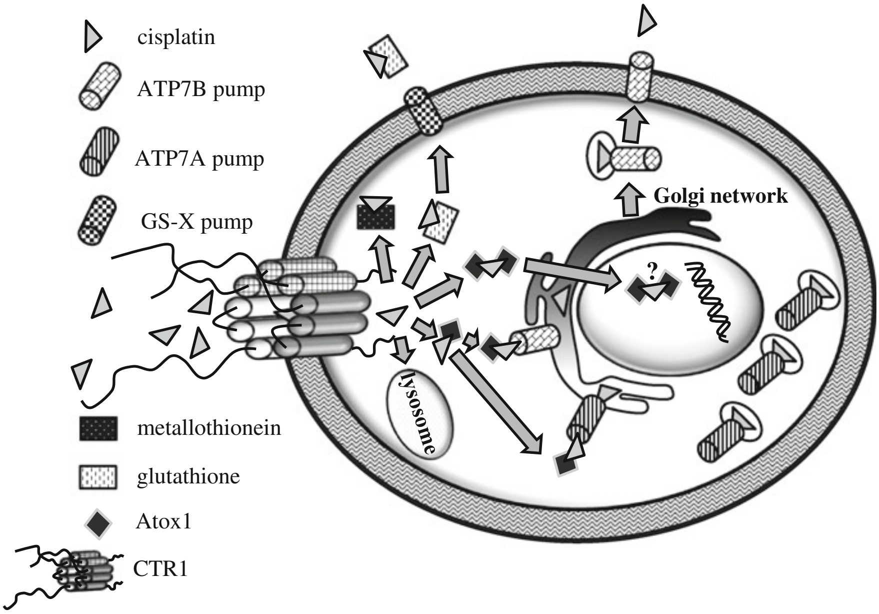

Fig. 3 Scheme of cisplatin trafficking. Cisplatin taken up by CTR1 is transported to lysosome and bound to glutathione (Shoeib and Sharp 2013), metallothionein (Zitka et al. 2013; Zhang et al. 2011; Knipp et al. 2007) or Atox1 (Palm-Espling et al. 2014; Palm et al. 2011). The platinum-GSH complex is exported by GS-X pump (Ishikawa and Aliosman 1993). Atox1 transfer platinum via ATP7A/B to Golgi network (GN) and induces structural changes that lead to the vesicular sequestration of the drug and trafficking of the ATP7A/B containing vesicles from the GN to peripheral sites for a drug efflux (Samimi et al. 2004). The mechanism of cisplatin entry to the cell nucleus has not been yet elucidated, but we assume, that the translocation of Atox1 dimer is possible

ototoxicity and also resistance to cisplatin have negative influence on the treatment results.

The cytotoxic effect of the platinum complexes is directly related to the quantity of drug that enters the cell (Fig. 3). Cisplatin, carboplatin and oxaliplatin are highly polar molecules, which do not diffuse across lipid membranes (Hall et al. 2008). Although cisplatin shares a little similarity with Cu ions in terms of physical properties, the cellular uptake of these substances is tightly connected. The Copper transporter 1 (CTR1), the main Cu influx transporter, has been found to mediate the cisplatin and its analogues transport into the cell via creation of membrane pore-like—homotrimer (Howell et al. 2010; Aller and Unger 2006). Cisplatin and copper are able to down-regulate CTR1 (its own influx transporter) expression (Holzer and Howell 2006). Several mechanisms of cisplatin influx were suggested. The diffusion of platinum through the pore after complete loss of ligands down the concentration gradient was proposed by Arnesano et al. (2007). Cisplatin can also bind to sulfur of CTR1 methionine extracellular N-terminus and after release of ammine ligands migrates through the pore by trans chelation reaction that pass the Cu or Pt based drug from one ring of methionine to the next one and eventually to the ring of cysteine (Wang et al. 2011; Larson et al. 2010). Although, the loss of ligands after coordination to methionine was also confirmed by Arnesano et al. (Arnesano and Natile 2008), it is believed that cisplatin has to keep the two ammine ligands to be active (Todd and Lippard 2009). It supports the thesis of multiple pathways of cisplatin influx into a cell. It must be also pointed out that only 1 % or less of the intravenously administrated cisplatin binds to DNA (Reedijk 1999). CTR2 was proved to be involved in cisplatin influx, too. Although CTR1 and CTR2 are structurally similar, CTR1 knockdown reduces Pt drug uptake, knockdown of CTR2 enhances cisplatin uptake (Abada and Howell 2010; Blair et al. 2009).

Trafficking of the endocytic vesicles, which absorb part of extracellular solution with all surrounding chemicals, is another potential pathway of Pt-based drugs into a cell. In addition, these vesicles can protect cisplatin and its analogues from cytosolic platinophiles like metallothioneins (MTs) and glutathione (GSH). Petis et al. described the mechanism of copper-stimulated clathrin-mediated endocytosis CTR1 (Petris et al. 2003).

2.2 *The Significance of Copper*

The cytoplasmic step on the pathway of copper ions involves small pathway specific metal binding proteins (metallochaperones) including antioxidant 1 (Atox1), copper chaperone for superoxide dismutase 1 (CCS) and cytochrome c oxidase (COX17). To our best knowledge, the possible platination of CCS and COX17 have not been proved (Suzuki et al. 2003; Burdon 1995). Totally different example is Atox1. The soluble cytosolic Cu chaperone Atox1 (previously known as HAH1) delivers Cu to a copper-transporting ATPases (ATP7A and ATP7B) in secretory vesicles by direct protein-protein interaction to facilitate copper excretion (Strausak et al. 2003; Walker et al. 2002; Banci et al. 2005). Copper binds to metal-binding sites (MXCXXC motif), which are highly conversed in Atox1 and also are presented in ATP7A/B N-terminus (Muller and Klomp 2009). Safaei et al. found out that the role of Atox1 in mechanism of Cu homeostasis is distinct from that involved cisplatin (Safaei et al. 2009). Although Atox1 facilitates Cu movement from CTR1 to ATP7A/B exporters leading to Cu efflux, it is involved in ATP7A mediated cisplatin accumulation in vesicular compartments. It was proved that cisplatin is able to bind to Atox1 CXXC motif and retains the two ammine ligands or induces Atox1 dimer formation (Arnesano et al. 2011). Atox1 was also identified as the copper-dependent transcription factor (Itoh et al. 2008). Copper can induce Atox1 nucleus translocation, binding to a novel cis element of the cyclin D1 promoter and transactivation, thereby promoting cell proliferation. Furthermore, copper overload was observed in various tumors (Crowe et al. 2013; Wang et al. 2010). It suggests that Atox1 play far more complex role in the regulation of the cell physiology. Question, which should be answered, is how Atox1 can exhibit two functions as a transcription factor and chaperone.

Export of Cu in mammalian cells involves two P-type ATPases (ATP7A and ATP7B). When extracellular copper concentrations are low, ATP7A and ATP7B are localized in the trans-Golgi network. Exposure to increased copper levels results in reversible re-localization of ATP7A to the plasma membrane and of ATP7B to intracellular vesicular compartments (Kalayda et al. 2008). ATP7A is involved in the transport of Cu from cytoplasm to trans-Golgi network, where Cu is bound to Cu-requiring enzymes, or export it from cell via the vesicular secretory pathway. On the other hand, Samimi et al. revealed, that ATP7A mediates cisplatin sequestration into compartments from which it is unable to reach the DNA and exert cytotoxicity (Samimi et al. 2004). The same mechanism of sequestration was also confirmed for oxaliplatin and carboplatin (Katano et al. 2002). The overexpression of ATP7B was proved to increase the resistance to cisplatin in prostate cancer (Komatsu et al. 2000). Katano et al. suggests that ATP7B enhances cisplatin efflux by sequestering it into the vesicular export pathway, which is known to efficiently export Cu (Katano et al. 2004).

2.3 Cytoplasmic Interactions

In plasma, where high chloride concentration occurs, cisplatin mostly remains in a native inactive form. Inside the cell chloride ions dissociate from the platinum due to the low chloride concentration, and are replaced by water molecules. Consequently positively charged platinum complex binds to the cell nucleophiles in DNA, RNA and proteins (Cohen and Lippard 2001). Inactivation by creation of stable Pt-thiol adduct is believed to be important Pt-based drug sink (Reedijk 1999). Pt was showed to bind to methionine, cysteine and histidine residues and have high affinity to most abundant cytosolic thiols, glutathione, and 50-times higher for metallothionein (Hagrman et al. 2003). The glutathione S-conjugates efflux can be mediated by some members of ATP-binding cassette (ABC) transporter superfamily (MRPs, multidrug resistance proteins), which regulate the sensitivity to chemotherapy including cisplatin and are in this case called the GS-X pump (Yamasaki et al. 2011; Zaman et al. 1995; Ishikawa and Aliosman 1993).

2.4 Reactive Oxygen Species and Apoptosis

Heavy metals are known to cause oxidative damaging of bio-molecules by initiating free radical mediated chain reaction resulting in lipid peroxidation, protein oxidation and oxidation of nucleic acids like DNA and RNA (Flora et al. 2013). Platinum drugs have been used in the chemotherapy of cancer for a long time, but the mechanism of its action is still not clear (Zitka et al. 2007). The most important

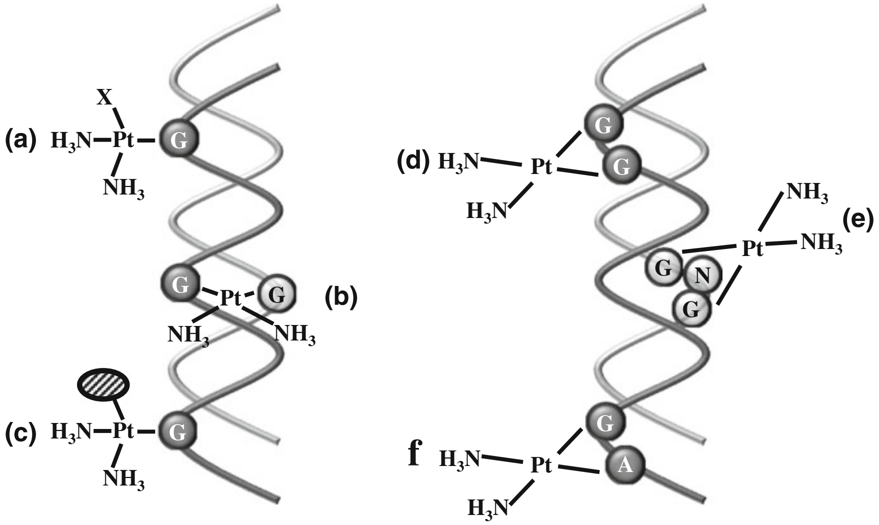

Fig. 4 Cisplatin DNA adducts: *a* Cisplatin bound monofunctionally to guanine (X—original chloride, or a hydroxyl group); *b* interstrand cross-link; *c* cisplatin guanine—protein cross-link; *d* GpG-intrastrand cross-link; *e* GpNpGintrastrand cross-link (N represents a base); *f* ApG-intrastrand cross-link. Adopted and modified according to Crul et al. (2002)

mechanism could be non-covalent DNA intercalation, formation of covalent DNA adducts, DNA-DNA cross-linking, DNA strand-breaks caused by inhibition of topoisomerase II, or the effect of the radicals (Stiborova et al. 2010) (Fig. 4). Platinum chemotherapy is beneficial for human epithelial cancers because the platinum agents induce DNA damage signaling, leading to initiation of cell cycle arrest and apoptosis, and ultimately to a tumor cell death (Guerrero-Preston and Ratovitski 2014). It was observed that oxaliplatin, its enantiomeric analogue, or cisplatin can migrate from one strand to another in double-helical DNA (Malina et al. 2013). Cisplatin, carboplatin and oxaliplatin are neutral platinum (II) complexes with two amine ligands and two additional ligands that can be aquated for further binding with DNA (Kao et al. 2013). Pt(IV) compounds are usually administered as prodrugs, which are reduced in the hypoxic environment of cancer cells to active Pt(II) species. Platinum(II) moiety forming in the process of binding Pt(IV) to genomic DNA causes cell death (Song et al. 2013).

Cisplatin induced reactive oxygen species (ROS) generation significantly caused loss of mitochondrial membrane potential in sensitive cells, but not in resistant cells to cisplatin. The induction of wild-type p53 can enhance cisplatin-induced apoptosis not only by inducing apoptosis regulator protein Bax but also by suppressing anti-apoptotic proteins through inhibition of Akt (protein kinase B) (Kim et al. 2013). By employing a panel of normal and cancer cell lines and the budding yeast *Saccharomyces cerevisiae* as model system, it was shown that exposure to cisplatin induces a mitochondrial-dependent ROS response that significantly enhances the cytotoxic effect caused by nuclear DNA damage. ROS generation is independent of the amount of cisplatin-induced nuclear DNA damage and occurs in mitochondria as a consequence of protein synthesis impairment. The contribution of cisplatin-induced mitochondrial dysfunction in determining its cytotoxic effect varies among cells and depends on mitochondrial redox status, mitochondrial DNA integrity and bioenergetic function (Marullo et al. 2013). In another study the effect of cisplatin and novel platinum(II) complexes, Pt-2(isopropylamine)(4)(berenil)(2), Pt-2 (piperazine)(4)(berenil)(2), Pt-2(2-picoline)(4)(berenil)(2), Pt-2(3-picoline)(4) (berenil)(2), Pt-2(4-picoline)(4)(berenil)(2), on the redox state of human leukemic T-cells line Molt-4 was investigated. Treatment of Molt-4 with the novel complexes has shown that all compounds enhance total ROS and superoxide anion generation as well as change the activity of antioxidant enzymes such as superoxide dismutase, catalase, glutathione peroxidase and glutathione reductase. Moreover, all the above-mentioned compounds cause a decrease in the level of non-enzymatic antioxidants such as GSH as well as vitamin C, E and A (Jarocka et al. 2013). In addition, the novel platinum (II) complexes enhanced expression of Bax and cytochrome c as well as decreased the expression of Bcl-2 and p53 protein. The novel platinum(II) complexes in comparison with cisplatin disturb redox status more intensively and lead to oxidative stress in Molt-4 cells (Jarocka et al. 2013).

2.5 Binding and Interaction of Platinum Drugs to DNA

Platinum drugs can diverse interact with DNA, the intercalation in double-stranded DNA and stacking on G-quadruplex DNA was observed in the case of $[PtCl_2(NH_3)(2\text{-aminonaphthalene})]$ (Gabano et al. 2013). Miriplatin (lipophilic platinum complex) selective accumulation in tumor tissue was detected. Determined platinum concentrations were about 50-fold higher in hepatocellular carcinoma than in non-tumor liver tissues. The platinum-DNA adduct levels were about 7.6-fold higher in hepatocellular carcinoma than in non-tumor liver tissues. And significant correlations between platinum concentrations and platinum-DNA adduct levels tumors were not observed (Yasui et al. 2013). Ampyplatin trans-$[PtCl_2(NH_3)_2(py)]$; py = pyridine) has much more higher antiproliferative activity than cis-$[PtCl(NH_3)_2(py)]^+$ and is comparable to cisplatin and can be efficiently accumulated in cancer cells. Ampyplatin binds to DNA and forms monofunctional adducts (Xu et al. 2013).

Platinum anticancer agents with phthalate leaving group show great cytotoxicity, less acute toxicity, good lipophilicity as well as better aqueous solubility (Sharma et al. 2013). Combination of cisplatin with other compounds can influence the platinum-DNA adducts. Antimetabolites can increase or decrease the number of platinum-DNA adducts. Taxanes can decrease the formation of platinum-DNA adducts, while topoisomerase I inhibitors enhance the number of adducts (Crul et al. 2002). After the treatment with cisplatin, the reduction in the contour length of the DNA fragments was observed (Mukhopadhyay et al. 2005).

Upregulation of HIF-1α (hypoxia-inducible factor 1) contributes to hypoxia-induced chemotherapeutic resistance in many cancer cells (Ye et al. 2012). The resistance is caused due to interaction with thiol-containing compounds (Monneret 2011) and sEH (soluble epoxide hydrolase) inhibition alleviate cisplatin-induced nephrotoxicity. The inhibition of sEH has anti-inflammatory and antiapoptotic properties (Liu et al. 2013).

2.6 Effects of Platinum Drugs on DNA Repair Mechanisms

Platinum-based derivatives improve survival of non-small cell lung cancer patients. The DNA base excision repair activity of the controls was significantly higher in comparison to cancer patients, but the activity of DNA nucleotide excision repair was nearly at the same level. The changes in the amount of single strand breaks and DNA cross-links during the therapy were observed. High level of single strand breaks was detected right after the chemotherapy (Fikrova et al. 2014). Excision repair cross-complementation group 1 (ERCC1) is a DNA repair enzyme that is frequently defective in non-small cell lung cancer (NSCLC). Its low expression correlates with platinum sensitivity and also modulated PARP1/2 (Poly (ADP-ribose) polymerase) sensitivity (Postel-Vinay et al. 2013). ERCC1 important in the removal of platinum induced DNA adducts and cisplatin resistance could be the prognostic factor in bladder cancer patients receiving platinum-based neoadjuvant chemotherapy (Ozcan et al. 2013). Platinum drugs in treatment of colorectal tumors have been limited via high incidence of tumor resistance. Platinum (IV) complex induces effective elimination of colon cancer in substantially lower doses than oxaliplatin (Blanarova et al. 2013). The signal-regulated kinases (ERK1 and ERK2) contribute to the proper execution of DNA damage response in terms of checkpoint activation and the repair of DNA lesions (Lin et al. 2013). p53 as a suppressor regulates the downstream effects of E2F1 (transcription factor) in cellular stress (DNA damage stress) (Zhou et al. 2013). The p38 MAPK (mitogen-activated protein kinase) inhibition in cooperation with cisplatin kills tumor cells, and could be employable for cancer treatment (Pereira et al. 2013).

2.7 Effects of Pt Nanoparticles

The effects of platinum nanoparticles (PtNPs) on different cell types are not fully understood. It was found that PtNPs trigger toxic effects on primary keratinocytes, decreasing cell metabolism, but these changes had no effects on cell viability or migration. Moreover, smaller PtNPs exhibited more deleterious effect on DNA stability than the big ones (Konieczny et al. 2013). The cytotoxic effect towards myoblast cancer cells (C2C12) of well-crystalline colloidal Pt quantum dots (Pt-QDs) was examined (Wahab et al. 2012). The detailed analyses of MTT assay revealed that in the presence of Pt-QDs, with increasing the incubation time, the number of cancer cells decreases. Moreover, with increasing concentration of Pt-QDs, the cancer cell death increases, confirming that the concentration of Pt-QDs has a significant role in controlling the number of cancer cells. Asharani et al. suggested p53 activation in PtNPs treated cells due to genotoxic stress, with subsequent activation of p21 leading to a proliferating cell nuclear antigen-mediated growth arrest in S phase and apoptosis (Asharani et al. 2010). Growth arrest in S phase can be caused not only by DNA damage, but also by DNA-polymerase inhibition, which exhibits high affinity to PtNPs and other metals (Pelletier et al. 1996; Popenoe and Schmaeler 1979). Cytotoxicity of PtNPs can be the result of its accumulation in lysosome and the release of Pt^{2+} (Asharani et al. 2010). The antioxidant properties of PtNPs were also investigated. Kajita et al. found that PtNPs decomposed H_2O_2 and consequently generated O_2 like catalase (Kajita et al. 2007). Further, Kim et al. (2012) confirmed that PtNPs act as antioxidants in murine osteoclasts and reduce oxidative stress induced by ovariectomy.

3 Conclusions

The platinum compounds show the wide range of the usage not only in the medicine. Although the therapeutic benefits the toxicity of platinum cannot be ignored. The cytotoxic effect of the platinum complexes is directly related to the quantity of drug that enters the cell. The positively charged platinum complex binds to the cell nucleophiles in DNA, RNA and proteins. Platinum metals interact with DNA by covalent intercalation and formation of DNA adducts. Also the formation of DNA adducts can be increased by some compounds. In this case the excision repair cross-complementation group 1 (ERCC1) is important in the removal of platinum induced DNA adducts. Platinum nanoparticles could be also employed to the tumor treatment. Finally we can conclude the cognitions of the interactions of PGEs on the cellular level could provide the better understanding to their cytotoxicity effects.

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References

Abada P, Howell SB (2010) Regulation of Cisplatin cytotoxicity by cu influx transporters. Met Based Drugs 2010:1–9

Ali I, Wani WA, Saleem K et al (2013) Platinum compounds: a hope for future cancer chemotherapy. Anti-Cancer Agents Med Chem 13:296–306

Aller SG, Unger VM (2006) Projection structure of the human copper transporter CTR1 at 6-A resolution reveals a compact trimer with a novel channel-like architecture. Proc Natl Acad Sci U S A 103:3627–3632

Arnesano F, Banci L, Bertini I et al (2011) Probing the interaction of Cisplatin with the human copper chaperone Atox1 by solution and in-cell NMR spectroscopy. J Am Chem Soc 133:18361–18369

Arnesano F, Natile G (2008) "Platinum on the road": interactions of antitumoral cisplatin with proteins. Pure Appl Chem 80:2715–2725

Arnesano F, Scintilla S, Natile G (2007) Interaction between platinum complexes and a methionine motif found in copper transport proteins. Angew Chem-Int Edit 46:9062–9064

Asharani PV, Xinyi N, Hande MP et al (2010) DNA damage and p53-mediated growth arrest in human cells treated with platinum nanoparticles. Nanomedicine 5:51–64

Banci L, Bertini I, Ciofi-Baffoni S et al (2005) An NMR study of the interaction between the human copper(I) chaperone and the second and fifth metal-binding domains of the Menkes protein. FEBS J 272:865–871

Blair BG, Larson C, Safaei R et al (2009) Copper transporter 2 regulates the cellular accumulation and cytotoxicity of cisplatin and carboplatin. Clin Cancer Res 15:4312–4321

Blanarova OV, Jelinkova I, Vaculova AH et al (2013) Higher anti-tumour efficacy of platinum(IV) complex LA-12 is associated with its ability to bypass M-phase entry block induced in oxaliplatin-treated human colon cancer cells. Cell Prolif 46:665–676

Burdon RH (1995) Superoxide and hydrogen-peroxide in relation to mammalian-cell proliferation. Free Radic Biol Med 18:775–794

Cohen SM, Lippard SJ (2001) Cisplatin: from DNA damage to cancer chemotherapy. Prog Nucl Res Mol Biol 67:93–130

Crowe A, Jackaman C, Beddoes KM et al (2013) Rapid copper acquisition by developing murine mesothelioma: decreasing bioavailable copper slows tumor growth, normalizes vessels and promotes T cell infiltration. PLoS ONE 8:1–14

Crul M, van Waardenburg R, Beijnen JH et al (2002) DNA-based drug interactions of cisplatin. Cancer Treat Rev 28:291–303

Crundwell FK, Moats MS, Ramachandran V et al (2011) Extractive metallurgy of nickel, cobalt and platinum-group metals overview. Extractive metallurgy of nickel, cobalt and platinum-group metals. doi:10.1016/b978-0-08-096809-4.10001-2

Dhahagani K, Mathan KS, Chakkaravarthi G et al (2014) Synthesis and spectral characterization of Schiff base complexes of Cu(II), Co(II), Zn(II) and VO(IV) containing 4-(4-aminophenyl) morpholine derivatives: Antimicrobial evaluation and anticancer studies. Spectr Acta Pt A-Mol Biomol Spectr 117:87–94

Eremia SAV, Vasilescu I, Radoi A et al (2013) Disposable biosensor based on platinum nanoparticles-reduced graphene oxide-laccase biocomposite for the determination of total polyphenolic content. Talanta 110:164–170

Fikrova P, Stetina R, Hrnciarik M et al (2014) DNA crosslinks, DNA damage and repair in peripheral blood lymphocytes of non-small cell lung cancer patients treated with platinum derivatives. Oncol Rep 31:391–396

Flora SJS, Shrivastava R, Mittal M (2013) Chemistry and pharmacological properties of some natural and synthetic antioxidants for heavy metal toxicity. Curr Med Chem 20:4540–4574

Florea AM, Büsselberg D (2011) Cisplatin as an anti-tumor drug: cellular mechanisms of activity, drug resistance and induced side effects. Cancers 3:1351–1371

Fu W, Li XH, Bao HL et al (2013) Synergistic effect of Bronsted acid and platinum on purification of automobile exhaust gases. Sci Rep 3:1–6

Furstner A (2009) Gold and platinum catalysis-a convenient tool for generating molecular complexity. Chem Soc Rev 38:3208–3221

Gabano E, Gama S, Mendes F et al (2013) Study of the synthesis, antiproliferative properties, and interaction with DNA and polynucleotides of cisplatin-like Pt(II) complexes containing carcinogenic polyaromatic amines. J Biol Inorg Chem 18:791–801

Galanski M, Jakupec MA, Keppler BK (2005) Update of the preclinical situation of anticancer platinum complexes: Novel design strategies and innovative analytical approaches. Curr Med Chem 12:2075–2094

Gheybi H, Niknejad H, Entezami AA (2014) Polymer-metal complex nanoparticles-containing cisplatin and amphiphilic block copolymer for anticancer drug delivery. Des Monomers Polym 17:334–344

Gitlin J, Lill R (2006) Special issue: cell biology of metals. Biochim Biophys Acta-Mol Cell Res 1763:577

Gitlin JD, Lill R (2012) Special issue: cell biology of metals. Biochim Biophys Acta-Mol Cell Res 1823:1405–1642

Gomez B, Palacios MA, Gomez M et al (2002) Levels and risk assessment for humans and ecosystems of platinum-group elements in the airborne particles and road dust of some European cities. Sci Total Environ 299:1–19

Graf N, Mokhtari TE, Papayannopoulos IA et al (2012) Platinum(IV)-chlorotoxin (CTX) conjugates for targeting cancer cells. J Inorg Biochem 110:58–63

Guerrero-Preston R, Ratovitski EA (2014) Cisplatin exposure of squamous cell carcinoma cells leads to modulation of the autophagic pathway. Autophagy: cancer, other pathologies, inflammation, immunity, infection, and aging, vol 1: Molecular mechanisms. Elsevier, San Diego. doi:10.1016/b978-0-12-405530-8.00017-0

Hagrman D, Goodisman J, Dabrowiak JC et al (2003) Kinetic study on the reaction of cisplatin with metallothionein. Drug Metab Dispos 31:916–923

Hall MD, Okabe M, Shen DW et al (2008) The role of cellular accumulation in determining sensitivity to platinum-based chemotherapy. In: Annual review of pharmacology and toxicology, vol 48. Annual Review of Pharmacology and Toxicology. Annual Reviews, Palo Alto, pp 495–535. doi:10.1146/annurev.pharmtox.48.080907.180426

Holzer AK, Howell SB (2006) The internalization and degradation of human copper transporter 1 following cisplatin exposure. Cancer Res 66:10944–10952

Hooda PS, Miller A, Edwards AC (2008) The plant availability of auto-cast platinum group elements. Environ Geochem Health 30:135–139

Howell SB, Safaei R, Larson CA et al (2010) Copper transporters and the cellular pharmacology of the platinum-containing cancer drugs. Mol Pharmacol 77:887–894

Ikeda S, Ohhata F, Miyoshi M et al (2000) Synthesis and reactions of palladium and platinum complexes bearing diphosphinidenecyclobutene ligands: a thermally stable catalyst for ethylene polymerization. Angew Chem-Int Edit 39:4512–4513

Ishikawa T, Aliosman F (1993) Glutathione-associated cis-diamminecichloroplatinum(II) metabolism and ATP-dependent efflux from leukemia-cells-molecular characterization of glutathione-platinum complex and its biological significance. J Biol Chem 268:20116–20125

Itoh S, Kim HW, Nakagawa O et al (2008) Novel role of antioxidant-1 (Atox1) as a copper-dependent transcription factor involved in cell proliferation. J Biol Chem 283:9157–9167

Jarocka I, Gegotek A, Bielawska A et al (2013) Effect of novel dinuclear platinum(II) complexes on redox status of MOLT-4 leukemic cells. Toxicol Mech Methods 23:641–649

Kajita M, Hikosaka K, Iitsuka M et al (2007) Platinum nanoparticle is a useful scavenger of superoxide anion and hydrogen peroxide. Free Radic Res 41:615–626

Kalayda GV, Wagner CH, Buss I et al (2008) Altered localisation of the copper efflux transporters ATP7A and ATP7B associated with cisplatin resistance in human ovarian carcinoma cells. BMC Cancer 8:1–12

Kao C, Chao A, Tsai CL et al (2013) Phosphorylation of signal transducer and activator of transcription 1 reduces bortezomib-mediated apoptosis in cancer cells. Cell Death Dis 4:1–12

Katano K, Kondo A, Safaei R et al (2002) Acquisition of resistance to cisplatin is accompanied by changes in the cellular pharmacology of copper. Cancer Res 62:6559–6565

Katano K, Safaei R, Samimi G et al (2004) Confocal microscopic analysis of the interaction between cisplatin and the copper transporter ATP7B in human ovarian carcinoma cells. Clin Cancer Res 10:4578–4588

Kim CW, Lu JN, Go SI et al (2013) p53 restoration can overcome cisplatin resistance through inhibition of Akt as well as induction of Bax. Int J Oncol 43:1495–1502

Kim W-K, Kim J-C, Park H-J et al (2012) Platinum nanoparticles reduce ovariectomy-induced bone loss by decreasing osteoclastogenesis. Exp Mol Med 44:432–439

Knipp M, Karotki AV, Chesnov S et al (2007) Reaction of Zn(7)Metallothionein with cis- and trans- Pt(N-donor)(2)Cl(2) anticancer complexes: trans-Pt(II) complexes retain their N-donor ligands. J Med Chem 50:4075–4086

Komatsu M, Sumizawa T, Mutoh M et al (2000) Copper-transporting P-type adenosine triphosphatase (ATP7B) is associated with cisplatin resistance. Cancer Res 60:1312–1316

Konieczny P, Goralczyk AG, Szmyd R et al (2013) Effects triggered by platinum nanoparticles on primary keratinocytes. Int J Nanomed 8:3963–3975

Larson CA, Adams PL, Jandial DD et al (2010) The role of the N-terminus of mammalian copper transporter 1 in the cellular accumulation of cisplatin. Biochem Pharmacol 80:448–454

Lin XZ, Yan J, Tang DM (2013) ERK kinases modulate the activation of PI3 kinase related kinases (PIKKs) in DNA damage response. Histol Histopath 28:1547–1554

Liu YM, Lu XD, Nguyen S et al (2013) Epoxyeicosatrienoic acids prevent cisplatin-induced renal apoptosis through a p38 mitogen-activated protein kinase-regulated mitochondrial pathway. Mol Pharmacol 84:925–934

Malina J, Natile G, Brabec V (2013) Spontaneous translocation of antitumor oxaliplatin, its enantiomeric analogue, and cisplatin from one strand to another in double-helical DNA. Chem Eur J 19:11984–11991

Manikandan M, Hasan N, Wu HF (2013) Platinum nanoparticles for the photothermal treatment of Neuro 2A cancer cells. Biomaterials 34:5833–5842

Marullo R, Werner E, Degtyareva N et al (2013) Cisplatin induces a mitochondrial-ROS response that contributes to cytotoxicity depending on mitochondrial redox status and bioenergetic functions. PLoS ONE 8:1–15

Monneret C (2011) Platinum anticancer drugs. From serendipity to rational design. Annal Pharm Franc 69:286–295

Mukhopadhyay R, Dubey P, Sarkar S (2005) Structural changes of DNA induced by mono- and binuclear cancer drugs. J Struct Biol 150:277–283

Muller PAJ, Klomp LWJ (2009) ATOX1: A novel copper-responsive transcription factor in mammals? Int J Biochem Cell Biol 41:1233–1236

Muscella A, Vetrugno C, Fanizzi FP et al (2013) A new platinum(II) compound anticancer drug candidate with selective cytotoxicity for breast cancer cells. Cell Death Dis 4:1–10

Oberoi HS, Nukolova NV, Kabanov AV et al (2013) Nanocarriers for delivery of platinum anticancer drugs. Adv Drug Deliv Rev 65:1667–1685

Ozcan MF, Dizdar O, Dincer N et al (2013) Low ERCC1 expression is associated with prolonged survival in patients with bladder cancer receiving platinum-based neoadjuvant chemotherapy. Urol Oncol-Semin Orig Investig 31:1709–1715

Palm-Espling ME, Lundin C, Bjorn E et al (2014) Interaction between the anticancer drug cisplatin and the copper chaperone Atox1 in human melanoma cells. Protein Pept Lett 21:63–68

Palm ME, Weise CF, Lundin C et al (2011) Cisplatin binds human copper chaperone Atox1 and promotes unfolding in vitro. Proc Natl Acad Sci USA 108:6951–6956

Pelletier H, Sawaya MR, Wolfle W et al (1996) A structural basis for metal ion mutagenicity and nucleotide selectivity in human DNA polymerase beta. Biochemistry 35:12762–12777

Pereira L, Igea A, Canovas B et al (2013) Inhibition of p38 MAPK sensitizes tumour cells to cisplatin-induced apoptosis mediated by reactive oxygen species and JNK. EMBO Mol Med 5:1759–1774

Petris MJ, Smith K, Lee J et al (2003) Copper-stimulated endocytosis and degradation of the human copper transporter, hCtr1. J Biol Chem 278:9639–9646

Piskulov M, Chiu C (2013) Kunming-PM’2012 5th international conference “Platinum metals in the modern industry, hydrogen energy and life maintenance of the future”. Platin Met Rev 57:143–147

Popenoe EA, Schmaeler MA (1979) Interaction of human DNA polymerase β with ions of copper, lead, and cadmium. Arch Biochem Biophys 196:109–120

Postel-Vinay S, Bajrami I, Friboulet L et al (2013) A high-throughput screen identifies PARP1/2 inhibitors as a potential therapy for ERCC1-deficient non-small cell lung cancer. Oncogene 32:5377–5387

Ravindra K, Bencs L, Van Grieken R (2004) Platinum group elements in the environment and their health risk. Sci Total Environ 318:1–43

Reedijk J (1999) Why does cisplatin reach guanine-N7 with competing S-donor ligands available in the cell? Chem Rev 99:2499–2510

Ruggiero A, Trombatore G, Triarico S et al (2013) Platinum compounds in children with cancer: toxicity and clinical management. Anticancer Drugs 24:1007–1019

Safaei R, Maktabi MH, Blair BG et al (2009) Effects of the loss of Atox1 on the cellular pharmacology of cisplatin. J Inorg Biochem 103:333–341

Samimi G, Safaei R, Katano K et al (2004) Increased expression of the copper efflux transporter ATP7A mediates resistance to cisplatin, carboplatin, and oxaliplatin in ovarian cancer cells. Clin Cancer Res 10:4661–4669

Sawyer TK (2006) Chemical biology and drug design: three-dimensional, dynamic, and mechanistic nature of two multidisciplinary fields. Chem Biol Drug Des 67:196–200

Sharma R, Rawal RK, Malhotra M et al (2013) Design, synthesis and in-vitro cytotoxicity of novel platinum (II) complexes with phthalate as the leaving group. Lett Drug Des Discov 10:872–878

Shoeib T, Sharp BL (2013) Monomeric cisplatin complexes with glutathione: coordination modes and binding affinities. Inorg Chim Acta 405:258–264

Sikorova L, Licbinsky R, Adamec V (2011) Platinum group elements from automobile catalysts in the environment. Chem Listy 105:361–366

Siriviriyanun A, Imae T, Nagatani N (2013) Electrochemical biosensors for biocontaminant detection consisting of carbon nanotubes, platinum nanoparticles, dendrimers, and enzymes. Anal Biochem 443:169–171

Song Y, Suntharalingam K, Yeung JS et al (2013) Synthesis and characterization of Pt(IV) fluorescein conjugates to Investigate Pt(IV) intracellular transformations. Bioconjugate Chem 24:1733–1740

Stiborova M, Poljakova J, Eckschlager T et al (2010) DNA and histone deacetylases as targets for neuroblastoma treatment. Interdiscip Toxicol 3:47–52

Strausak D, Howie MK, Firth SD et al (2003) Kinetic analysis of the interaction of the copper chaperone Atox1 with the metal binding sites of the Menkes protein. J Biol Chem 278:20821–20827

Suzuki C, Daigo Y, Kikuchi T et al (2003) Identification of COX17 as a therapeutic target for non-small cell lung cancer. Cancer Res 63:7038–7041

Todd RC, Lippard SJ (2009) Inhibition of transcription by platinum antitumor compounds. Metallomics 1:280–291

Wahab R, Yang YB, Umar A et al (2012) Platinum quantum dots and their cytotoxic effect towards myoblast cancer cells (C2C12). J Biomed Nanotechnol 8:424–431

Walker JM, Tsivkovskii R, Lutsenko S (2002) Metallochaperone Atox1 transfers copper to the NH2-terminal domain of the Wilson's disease protein and regulates its catalytic activity. J Biol Chem 277:27953–27959

Wang F, Jiao P, Qi M et al (2010) Turning tumor-promoting copper into an anti-cancer weapon via high-throughput chemistry. Curr Med Chem 17:2685–2698

Wang XH, Du XB, Li HY et al (2011) The effect of the extracellular domain of human copper transporter (hCTR1) on cisplatin activation. Angew Chem-Int Edit 50:2706–2711

Wang YJ, Li XZ (2012) Health risk of platinum group elements from automobile catalysts. In: Changgen F, Shengcai L (eds) 2012 International symposium on safety science and technology, vol 45. Procedia Engineering. Elsevier Science Bv, Amsterdam, pp 1004–1009. doi:10.1016/j.proeng.2012.08.273

Xu DC, Min YZ, Cheng QQ et al (2013) Chemical and cellular investigations of trans-ammine-pyridine-dichlorido-platinum(II), the likely metabolite of the antitumor active cis-diammine-pyridine-chorido-platinum(II). J Inorg Biochem 129:15–22

Yamasaki M, Makino T, Masuzawa T et al (2011) Role of multidrug resistance protein 2 (MRP2) in chemoresistance and clinical outcome in oesophageal squamous cell carcinoma. Br J Cancer 104:707–713

Yang L, Wang GC, Liu YJ (2013) An acetylcholinesterase biosensor based on platinum nanoparticles-carboxylic graphene-nafion-modified electrode for detection of pesticides. Anal Biochem 437:144–149

Yasui K, Takashima H, Miyagawa M et al (2013) Selective accumulation of platinum and formation of platinum-DNA adducts in hepatocellular carcinoma after transarterial chemo-embolization with miriplatin. Hepatol Res 43:1093–1099

Ye MX, Zhao YL, Li Y et al (2012) Curcumin reverses cis-platin resistance and promotes human lung adenocarcinoma A549/DDP cell apoptosis through HIF-1 alpha and caspase-3 mechanisms. Phytomedicine 19:779–787

Zaman GJR, Lankelma J, Vantellingen O et al (1995) Role of glutathione in the export of compounds from cells by the multidrug-resistance-associated protein. Proc Natl Acad Sci USA 92:7690–7694

Zereini F, Alt F, Messerschmidt J et al (2005) Concentration and distribution of heavy metals in urban airborne particulate matter in Frankfurt am main, Germany. Environ Sci Technol 39:2983–2989

Zereini F, Wiseman C, Puttmann W (2007) Changes in palladium, platinum, and rhodium concentrations, and their spatial distribution in soils along a major highway in Germany from 1994 to 2004. Environ Sci Technol 41:451–456

Zhang GX, Hu WB, Du ZF et al (2011) A comparative study on interactions of cisplatin and ruthenium arene anticancer complexes with metallothionein using MALDI-TOF-MS. Int J Mass Spectrom 307:79–84

Zhou Z, Cao JX, Li SY et al (2013) p53 Suppresses E2F1-dependent PLK1 expression upon DNA damage by forming p53-E2F1-DNA complex. Exp Cell Res 319:3104–3115

Zitka O, Huska D, Krizkova S et al (2007) Study of binding of platinum based cytostatics to DNA structure; Influence of glutathione. Tumor Biol 28:123–123

Zitka O, Kominkova M, Skalickova S et al (2013) Single amino acid change in metallothionein metal-binding cluster influences interaction with cisplatin. Int J Electrochem Sci 8:2625–2634

Part V

Human Health Exposures to PGE and Possible Risks

Biomonitoring of Platinum Group Elements (PGEs) in Occupational Medicine

Iavicoli Ivo and Leso Veruscka

Abstract Platinum, palladium, rhodium and iridium are platinum group elements (PGEs) employed in several industrial, chemical, and electronic applications and as active catalyst materials in automotive converters. However, despite the widespread use of these metals and their increasing emission into the environment due to the abrasion of catalytic devices, little is known of their toxic effects. Considerable concern has therefore arisen over the potential health risks for the general population and particularly for workers exposed to PGEs during production and recycling activities or via traffic emissions. Consequently, biological monitoring is important in order to assess PGE exposure, early effects and susceptibility factors so that occupational risks can be adequately evaluated and managed. This chapter aims to evaluate potential biomarkers of occupational PGE exposure and discuss issues regarding future research aimed at determining indicators of early PGE effects and susceptibility, and focus on the relevance and feasibility of these potential biomarkers in occupational health practice.

Keywords Platinum group elements (PGEs) · Platinum · Palladium · Rhodium · Iridium · Biological monitoring · Biomarkers of exposure · Biomarkers of effect · Biomarkers of susceptibility

1 Introduction

Among the platinum group elements (PGEs) we find platinum (Pt), palladium (Pd), rhodium (Rh) and iridium (Ir) that are rare, transition metals with similar physicochemical properties that include high resistance to wear, tarnish and chemical attack, stable electrical properties and outstanding catalytic and high temperature

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performance. Worldwide PGE production has steadily increased since the 1970s to meet demand for use in a wide variety of industrial, chemical, electronic, dental and jewelry applications (Johnsonn Matthey Publications 2013). However, PGEs are principally used as active catalyst materials in automotive catalytic converters. In fact, it is estimated that autocatalyst demand will account for 37, 72 and 79 % of the total worldwide gross demand for Pt, Pd, and Rh respectively in 2013 (Johnsonn Matthey Publications 2013).

Catalytic converters are manufactured with a ceramic or metal substrate, covered in an alumina washcoat on whose surface varying proportions of PGEs, mainly Pt, Pd, and Rh, are highly dispersed. Their use has reduced emission into the atmosphere of hazardous combustion engine pollutants by over 90 % since harmful automobile exhaust components such as carbon monoxide, hydrocarbons, and nitrogen oxides (NOx) are oxidized and reduced to harmless carbon dioxide, water and nitrogen (Wang and Li 2012). More recently Ir has been added to automotive converters, as the so-called “DeNO*x*” catalysator, in order to drastically reduce NO emission in lean burning engine exhausts (Ravindra et al. 2004).

Although catalytic converters are beneficial for air quality, they have nevertheless become the main source of anthropogenic PGE pollution in the environment. During engine operation, mechanical abrasion and deterioration within the catalytic converters due to rapidly changing oxidative/reductive chemical conditions, mechanical friction, stresses, sintering and thermal shock can lead to the release of PGEs into the environment (Palacios et al. 2000; Moldovan et al. 2002). Once dispersed in the atmosphere, PGEs can be adsorbed on air suspended matter (Gómez et al. 2002; Wiseman and Zereini 2009; Zereini et al. 2001, 2005, 2012), and subsequently accumulate in road dusts (Djingova et al. 2003; Jarvis et al. 2001; Mathur et al. 2011) and soils (Hooda et al. 2007, 2008; Zereini et al. 2007). This may then cause to bioaccumulation in living organisms such as vegetation (Niemela et al. 2004; Pino et al. 2010) and animals (Ek et al. 2004; Marcheselli et al. 2010).

Despite the rise in environmental PGE levels, a more widespread industrial use of PGEs and an increasing likelihood of human exposure, little is known of the toxicokinetics and adverse toxic effects of these metals. Consequently, there is growing concern over the potential health risks for the general population and particularly for workers exposed to these metals during production and recycling activities or on account of prolonged exposure to traffic emissions. In this context, biological monitoring defined as “the repeated, controlled measurement of chemical or biochemical markers in fluids, tissues or other accessible samples from subjects exposed or exposed in the past or to be exposed to chemical, physical or biological risk factors in the workplace” must therefore contribute to exposure prevention (Manno et al. 2010). As occurs with other occupational xenobiotics, occupational health risks are intrinsically dependent on the external exposure levels, bioavailability, and toxicological behavior of PGEs once these metals are adsorbed into the organism. Therefore, it is important to identify biological indicators that can assess exposure, early effects and susceptibility factors so that adequate occupational risk assessment and management processes can be established.

This chapter evaluates potential PGE exposure biomarkers in occupational settings and discusses a number of essential issues that may provide a significant stimulus for future research aimed at determining biological indicators of early PGE effects and susceptibility. It also provides a critical evaluation of the relevance of these potential biomarkers and the feasibility of using them in biological monitoring programs for future epidemiologic research and occupational health practice.

2 Biomarkers of Exposure

A biomarker of exposure is defined as a chemical, its metabolite or as the product of an interaction between a chemical and a target molecule or macromolecule that is measured in a compartment or fluid of an organism. In occupational health practice, exposure biomarkers play a very important role since they make it possible to assess exposure by all routes, taking into account inter-individual variability in absorption, metabolism and excretion, individual workload and recent versus past exposure (Manno et al. 2010). The following sections will provide a summary of current exposure biomarkers that have been investigated in biological matrices collected from occupationally-exposed subjects, and which are suitable to be employed in occupational health practice.

2.1 Blood and Serum

2.1.1 Platinum

Pt concentrations in the blood and serum of occupationally-exposed subjects have been shown to be suitable internal exposure indicators for measuring the total amount of metal adsorbed by the body following an external exposure. In fact, most of the studies reviewed, reveal significant differences between occupationally-exposed subjects and non-exposed controls, and a positive correlation between environmental exposure levels and Pt concentrations in these biological matrices (Table 1). Workers engaged in the manufacturing and recycling of Pt-containing catalysts had mean blood and serum Pt levels significantly higher than those reported for non-occupationally exposed subjects (Schaller et al. 1992). Similarly, a significant rise in Pt content in the blood and plasma of occupationally-exposed subjects compared to non-exposed controls was reported by Messerschmidt et al. (1992).

Mean Pt concentrations in whole blood samples collected from precious metal workers differed significantly from those found in the blood of motorway maintenance workers and of college employees enrolled as controls (Farago et al. 1998). This finding may be due to different levels and conditions of exposure, e.g. indoor vs outdoor workplace settings for Pt refinery and motorway maintenance workers, respectively. The Pt concentrations found in maintenance workers and employees

Table 1 Biological monitoring of Pt, Pd, Rh and Ir in blood and serum of occupationally exposed subjects

Workers (number)	Environmental exposure	Blood and/or serum concentrations Mean (±sd) levels (ng/l, if not indicated otherwise)	References
Platinum			
Manufacturing and recycling of Pt containing catalysts (40), non-exposed controls (13)	Median air concentrations: 3.1, 3.8, 1.8 μg/m^3 in production, recycling and mechanical treatment sections, respectively	Blood: 39 (range 2-180) (PS); 125 (MS) Serum: 39 (range 4-280) (PS); 75 (MS) Non-exposed subjects (blood and serum): 0.8-6.9	Schaller et al. (1992)
Occupationally exposed subjects (task not specified), non-exposed controls	-	Blood (exposed workers): 81 (range 32–180) Serum (exposed workers): 170 (range: 95 −280) Blood and serum (controls): ≤0.8–6.9	Messerschmidt et al. (1992
Pt refinery (7), motorway maintenance (10), college employees as controls (5)	Mean Pt concentrations in soil and dust at major road intersections: 20.8; major roads 12.9; intermediate roads 1.93; minor roads 2.29 ng/g	Blood (refinery workers): 246 (range: 152–423) Blood (motorway maintenance workers): 145 (range: 126–158); Blood (college employees): 129 (range: 115–139)	Farago et al. (1998)
Catalyst (10), subjects with persistent low-exposure (30), non-exposed subjects (10)	Soluble Pt in air: up to 3700 in high exposure; up to 8.6 in low exposure; <0.1 ng/m^3 in control areas. Concentrations of insoluble Pt were 10 fold higher	Serum (high exposed catalyst operators): ~75 Serum (low-exposure subjects): ~20 Serum: non-exposed subjects: ~10	Merget et al. (2000)
Catalyst production (4), non-exposed controls (2)	–	Serum (exposed workers): range 10–290 Serum (controls): range <10-640	Merget et al. (2002)
Catalyst plant: production sectors (12), administrative service (3), external controls (10)	Mean Pt concentrations in PM$_{10}$–area sampling: 0.02 (SSD); 1.71 (CD); 0.23 (CCD); 0.18 (RD); 0.008 (AS); <1.8x 10^{-5} μg/m^3 (EC)	Blood: 110 (SSD); 2900 (CD); 110 (CCD) 210 (RD); 50 (AS); 6 (EC) Serum: 80 (SSD); 1550 (CD); 40 (CCD)	Petrucci et al. (2004)
		150 (RD); 30 (AS); 2 (EC)	

(continued)

Table 1 (continued)

Workers (number)	Environmental exposure	Blood and/or serum concentrations Mean (±sd) levels (ng/l, if not indicated otherwise)	References
Catalyst plant: production sector (84), quality control (17), internal controls (21), external controls (25)	Mean Pt concentrations in PM_{10}–area sampling: 0.02 (SSD); 1.21 (CD); 0.18 (PCD); 0.24 (RS); 0.02 (RFD); 0.01 (remaining sectors: AL, AS); $<0.02x10^{-3}$ μg/m^3 (EC) Personal sampling: 0.41, 2.70, 0.05, 0.68, 0.06, 0.01 μg/m^3 in the above departments, respectively; N.A. (EC)	Blood: 70 ± 40 (SSD1), 140 ± 80 (SSD2); 380 ± 310 (CD) 170 ± 170 (PCD); 140 ± 110 (RS); 240 ± 170 (RFD); 130 ± 60 (AL); 180 ± 120 (AS); 10 ± 2 (EC)	Petrucci et al. (2005)
Catalyst plant: production sector (90), quality control (16), internal controls (16), external controls (25)	Mean Pt concentration of in PM_{10} – area sampling: 0.02 ± 0.01 (SSD); 1.21 ± 0.74 (CD); 0.18 ± 0.009 (CCD); 0.24 ± 0.08 (RD); 0.02 ± 0.01 (AD); $<0.02x10^{-3}$ μg/m^3 (EC) Personal sampling: 0.41 ± 0.08, 2.70 ± 1.52, 0.05 ± 0.05, 0.68 ± 0.14, 0.01 ± 0.002 μg/m^3 in the above departments, respectively; N.A. (EC)	Blood: 100 ± 70 (SSD); 380 ± 310 (CD); 170 ± 170 (CCD); 190 ± 140 (RD); 130 ± 60 (QC); 180 ± 120 (AD); 10 ± 2 (EC).	Cristaudo et al. (2007)
Palladium			
Catalyst plant: production sectors (12), administrative service (10), external controls (10)	Mean Pd concentrations in PM_{10} - area sampling: 0.06 (SSD); 0.094 (CD); 2.1 (CCD); 10.6 (RD); 0.006 (AS); $<0.02x\ 10^{-3}$ μg/m^3 (EC)	Blood: 740 (SSD); 2230 (CD); 720 (CCD); 540 (RD); 10 (AS); <10 (EC). Serum: 410 (SSD); 710 (CD); 650 (CCD); 410 (RD); 10 (AS); <7 (EC)	Petrucci et al. (2004)
Catalyst plant: production sector (84), quality control (17), internal controls (21), external controls (25)	Mean Pd concentrations in PM_{10} – area sampling: 0.05 (SSD); 0.17 (CD); 4.05 (PCD); 7.70 (RS); 0.35 (RFD); 0.04 (remaining sectors: AL, AS); $<0.02x\ 10^{-3}$ (EC) μg/m^3.	Blood: 950 ± 610 (SSD); 1020 ± 820 (CD); 1030 ± 790 (PCD); 2020 ± 1230 (RS); 850 ± 490 (RFD);	Violante et al. (2005)

(continued)

Table 1 (continued)

Workers (number)	Environmental exposure	Blood and/or serum concentrations Mean (±sd) levels (ng/l, if not indicated otherwise)	References
	Personal sampling: 0.12, 0.03, 1.44, 5.75, 0.56, 0.03 µg/m^3, in the above departments, respectively; N.A. (EC)	880 ± 330 (AL); 890 ± 670 (AS); 50 ± 20 (EC)	
Catalyst plant: production sector (90), quality control (16), internal controls (16), external controls (25)	Mean Pd concentrations in PM$_{10}$ – area sampling: 0.05 ± 0.01 (SSD); 0.17 ± 0.08 (CD); 4.05 ± 2.38 (CCD); 7.70 ± 4.15 (RD); 0.04 ± 0.03 (AD); <0.02x 10^{-3} (EC) µg/m^3. Personal sampling: 0.12 ± 0.06, 0.03 ± 0.02, 1.76 ± 2.41, 5.75 ± 3.04, 0.03 ± 0.002, µg/m^3 in the above departments, respectively; N.A. (EC)	Blood: 670 ± 450 (SSD); 1020 ± 820 (CD); 1030 ± 790 (CCD); 1310 ± 1040 (RD); 880 ± 330 (QC); 910 ± 640 (AD); 50 ± 20 (EC).	Cristaudo et al. (2007)
Rhodium			
Catalyst plant: production sectors (12), administrative service (10), external controls (10)	Mean Rh concentrations in PM$_{10}$ - area sampling: 1.0x10^{-3} (SSD); 2.0x10^{-3} (CD); 3.0x10^{-3} (CCD); 1.0x10^{-3} (RD); 1.0x10^{-3} (AS); <0.006x10^{-3} (EC) µg/m^3.	Blood: 110 (SSD); 2940 (CD); 210 (CCD); 150 (RD); 140 (AS); <3 (EC). Serum: 130 (SSD); 1360 (CD); 170 (CCD); 110 (RD); 100 (AS); <2 (EC).	Petrucci et al. (2004)
Catalyst plant: production sector (90), quality control (16), internal controls (16), external controls (25)	Mean Rh concentrations in PM$_{10}$ – area sampling: 1.0x10^{-3} (SSD); 2.0x10^{-3} (CD); 3.0x10^{-3} (CCD); 1.0x10^{-3} (RD); 1.0x10^{-3} (AD); <0.006 x 10^{-3} (EC) µg/m^3. Personal sampling: 1.0x10^{-3}, 35.0x10^{-3}, 3.0x10^{-3}, 1.0x10^{-3}, 0.1x10^{-3}, µg/m^3 in the above departments, respectively, N.A. (EC)	Blood: 110 ± 10 (SSD); 290 ± 15 (CD); 90 ± 4 (CCD); 200 ± 10 (RD); 180 ± 11 (QC); 140 ± 9 (AD); 2 ± 1 (EC)	Cristaudo et al. (2007)

(continued)

Table 1 (continued)

Workers (number)	Environmental exposure	Blood and/or serum concentrations Mean (±sd) levels (ng/l, if not indicated otherwise)	References
IRIDIUM			
Catalyst plant: production sectors (12), administrative service (10), external controls (10)	Mean Ir concentrations in PM_{10} - area sampling: $2.0x10^{-3}$ (SSD); $0.6x10^{-4}$ (CD); $0.07x10^{-3}$ (CCD); $0.09x10^{-3}$ (RD); $0.05x10^{-3}$ (AS); $<0.006x10^{-3}$ (EC) μg/m^3.	Blood: 20 (SSD); 2050 (CD); 30 (CCD); 150 (RD); 40 (AS); 1 (EC). Serum: 20 (SSD); 740 (CD); 30 (CCD); 160 (RD); 20 (AS).; 1 (EC).	Petrucci et al. (2004)
Catalyst plant: production sector (90), quality control (16), internal controls (16), external controls (25)	Mean Ir concentrations in PM_{10} – area sampling: $2.0x10^{-3}$ (SSD); $0.6x10^{-3}$ (CD); $0.07x10^{-3}$ (CCD); $0.09x10^{-3}$ (RD); $0.05x10^{-3}$ (AD); <0.006 x 10^{-3} (EC) μg/m^3. Personal sampling: $2.0x10^{-3}$, $0.2x10^{-3}$, 0.8 $x10^{-3}$, $1.0x10^{-3}$, $0.06x10^{-3}$ μg/m^3 in the above departments, respectively; N.A. (EC)	Blood: 20 ± 10 (SSD); 210 ± 15 (CD); 30 ± 2 (CCD); 160 ± 10 (RD); 50 ± 3 (QC); 40 ± 2 (AD); 1 ± 0.8 (EC).	Cristaudo et al. (2007)

AD, administrative department; AL, analytical laboratory; AS, administrative service; CCD, chemical catalyst department; CD, coating department; EC, external controls; MS, mechanical section; PCD, process catalyst department; PS, production section; PM, particulate matter; RFD, refinery department; RD, recycling department; RS, recycling service; SD, standard deviation; SSD, salt and solution department may represent background levels influenced respectively by working on a motorway in a rural area or living/working in urban areas with high traffic fumes. However, as the Pt level in blood was not correlated with blood lead concentrations, the authors failed to conclude that traffic emissions were the primary source of Pt. Concentrations of Pt determined in serum samples collected from workers of a catalyst production plant revealed a significant difference between the high-exposed category of catalyst operators and the low-exposed and control groups (Merget et al. 2000). However, in a subsequent study, the same authors failed to observe that Pt concentrations in serum reflected occupational exposure to the metal (Merget et al. 2002).

Several studies evaluated environmental Pt exposure in a plant engaged in the production, recovery, and recycling of catalytic converters and the Pt concentration in the blood and serum of exposed workers (Petrucci et al. 2004, 2005; Cristaudo et al. 2007). In line with the preliminary results reported by Petrucci et al. (2004), the other two studies observed the highest environmental concentrations of Pt in the coating department where Pt salt solutions were used to coat catalytic supports (Petrucci et al. 2005; Cristaudo et al. 2007). In keeping with the environmental scenario, the highest mean levels of Pt in blood and serum were detected in workers from this department. Although not directly exposed to airborne Pt, workers employed in administrative sectors presented levels of contaminant similar to those found in workers involved in the production processes and higher than those of external controls (Petrucci et al. 2004, 2005; Cristaudo et al. 2007). This fact may have been due to the increased baseline pollution occurring inside the factory. Interestingly, the authors suggested that blood Pt concentrations were a good indication of long-term exposure to the metal and provided information on Pt body burden (Petrucci et al. 2005; Cristaudo et al. 2007).

2.1.2 Palladium

Workers from both the production sectors and administrative services of a catalyst production and recycling plant were monitored for environmental Pd exposure and for concentrations of this metal in blood and serum (Petrucci et al. 2004; Violante et al. 2005; Cristaudo et al. 2007) (Table 1). Results generally confirmed the pattern of environmental contamination and revealed a Pd body burden for all workers, including those not directly involved in the production processes, that was consistently higher than in external controls. The highest mean Pd blood concentrations were found in the departments where the processes to recover spent chemical catalysts and those where either metal salt solutions were adsorbed on carriers or used to coat converters induced the greatest environmental dispersion of the metal (Violante et al. 2005; Cristaudo et al. 2007). As in the case of Pt, blood Pd concentrations probably well represented the body burden of the metal most affected by homeostatic processes and were thus less effective in assessing the current occupational exposure levels (Cristaudo et al. 2007).

2.1.3 Rhodium

Rh biomonitoring data obtained from subjects employed in the production or administrative departments of a catalyst plant showed significantly higher blood and serum concentrations than in external controls (Petrucci et al. 2004; Cristaudo et al. 2007) (Table 1). The highest mean Rh value was detected in blood from workers of the coating department where the highest environmental Rh exposure was detected by personal sampling (Cristaudo et al. 2007). Administrative workers had a mean blood Rh level in the same order of magnitude as that found in workers exposed in other production sites, thus suggesting that Rh pollution was also widespread in areas of the plant that were not directly involved in manipulation of the metal.

2.1.4 Iridium

Blood and serum Ir concentrations in workers of a catalyst refinery plant were significantly higher than those in external controls with the highest levels being found in subjects engaged in the coating department (Petrucci et al. 2004; Cristaudo et al. 2007) (Table 1). Unfortunately, in these two studies biological Ir results did not well reflect environmental levels. In fact, even if the highest mean airborne Ir concentrations were recorded in the salt and solution department, workers in this sector surprisingly showed the lowest average Ir blood and serum levels (Petrucci et al. 2004; Cristaudo et al. 2007). This finding suggests that other factors maybe related to the workplace and job conditions, and individual factors may also play a role in influencing biological monitoring results.

2.2 Urine

2.2.1 Platinum

The role of urinary Pt concentration as a useful biomarker of occupational exposure has been reported in several studies carried out on workers exposed in catalyst plants (Schaller et al. 1992; Messerschmidt et al. 1992; Farago et al. 1998; Schierl et al. 1998; Petrucci et al. 2004, 2005; Cristaudo et al. 2007) or to vehicular traffic (Iavicoli et al. 2004, 2007; Óvári et al. 2007) (Table 2). Schaller et al. (1992) found that Pt concentrations in urine samples from workers employed in the manufacturing and recycling of Pt containing catalysts were higher than in non-exposed controls. The highest mean concentration was found in workers in the production department, while lower mean concentrations were observed in workers involved in the recycling and mechanical treatment departments. A significant correlation was found between Pt levels in blood, serum, and urine, but not with the median airborne Pt concentrations in the three aforementioned departments. The same

Table 2 Biological monitoring of Pt, Pd, Rh and Ir concentrations in urine of occupationally exposed subjects

Workers (number)	Environmental exposure	Urine concentrations	References
		Mean (±SD) levels (ng/L, if not indicated otherwise)	
Platinum			
Manufacturing and recycling of Pt containing catalysts (40), non-exposed controls (13)	Median air concentrations: 3.1, 3.8, 1.8 µg/m^3 in production, recycling and mechanical treatment sections, respectively	Production section:1260; recycling section: 330; mechanical section: 430 (global range 10–2900) Non-exposed subjects: 0.4–14.3	Schaller et al. (1992)
Occupationally exposed subjects (task not specified), non-exposed controls	–	Exposed workers: 680 (range: 21–2900) Controls: 3.5 (range: 0.5–14.3)	Messerschmidt et al. (1992)
Pt refinery (7), motorway maintenance (10), college employees as controls (5)	Mean Pt concentrations in soil and dust at major road intersections: 20.8; major roads 12.9; intermediate roads 1.93; minor roads 2.29 ng/g	Refinery workers: 470 ng/g creatinine (range: 210–1180); Motorway workers: 58 ng/g creatinine (range: 22–135); College employees: 113 ng/g creatinine (range 48–224)	Farago et al. (1998)
Pt refinery and catalyst production company (22), non-exposed controls (12)	Mean air concentrations: 1.1 (range 0.2–3.4) (stationary); 2.5 µg/m^3 (range: 0.8–7.5) (personal sampling). Mean air concentration (controls): <0.007 µg/m^3	High exposure group: 170–6270 ng/g creatinine; Former high exposure group: 10–170 ng/g creatinine; Low exposure group: 16–230 ng/g creatinine; Controls: 1–12 ng/g creatinine	Schierl et al. (1998)
Catalyst plant: production sectors (12), administrative service (3), external controls (10)	Mean Pt concentrations in PM$_{10}$—area sampling: 0.02 (SSD); 1.71 (CD); 0.23 (CCD); 0.18 (RD); 0.008 (AS); <1.8 × 10^{-5} µg/m^3 (EC).	405 (SSD); 2065 (CD); 145(CCD); 130 (RD); 155 (AS); 3 (EC)	Petrucci et al. (2004)

(continued)

Table 2 (continued)

Workers (number)	Environmental exposure	Urine concentrations	References
		Mean (±SD) levels (ng/L, if not indicated otherwise)	
Catalyst plant: production sector (84), quality control (17), internal controls (21), external controls (25)	Mean Pt concentrations in PM_{10}—area sampling: 0.02 (SSD); 1.21 (CD); 0.18 (PCD); 0.24 (RS); 0.02 (RFD); 0.01 (remaining sectors: AL, AS); $<0.02 \times 10^{-3}$ μg/m^3 (EC)	Blood: 70 ± 40 (SSD1), 140 ± 80 (SSD2); 380 ± 310 (CD); 170 ± 170 (PCD); 140 ± 110 (RS); 240 ± 170 (RFD); 130 ± 60 (al); 180 ± 120 (AS); 10 ± 2 (EC)	Petrucci et al. (2005)
	Personal sampling: 0.41, 2.70, 0.05, 0.68, 0.06, 0.01 μg/m^3 in the above departments, respectively; N.A. (EC)		
Catalyst plant: production sector (90), quality control (16), internal controls (16), external controls (25)	Mean Pt concentration of in PM_{10}—area sampling: 0.02 ± 0.01 (SSD); 1.21 ± 0.74 (CD); 0.18 ± 0.009 (CCD); 0.24 ± 0.08 (RD); 0.02 ± 0.01 (AD); $<0.02 \times 10^{-3}$ μg/m^3 (EC)	Blood: 100 ± 70 (SSD); 380 ± 310 (CD); 170 ± 170 (CCD); 190 ± 140 (RD); 130 ± 60 (QC); 180 ± 120 (AD); 10 ± 2 (EC)	Cristaudo et al. (2007)
	Personal sampling: 0.41 ± 0.08, 2.70 ± 1.52, 0.05 ± 0.05, 0.68 ± 0.14, 0.01 ± 0.002 μg/m^3 in the above departments, respectively; N.A. (EC)		
Palladium			
Catalyst plant: production sectors (12), administrative service (10), external controls (10)	Mean Pd concentrations in PM_{10}—area sampling: 0.06 (SSD); 0.094 (CD); 2.1 (CCD); 10.6 (RD); 0.006 (AS); $<0.02 \times 10^{-3}$ μg/m^3 (EC)	Blood: 740 (SSD); 2230 (CD); 720 (CCD); 540 (rd); 10 (AS); <10 (EC).	Petrucci et al. (2004)
		Serum: 410 (SSD); 710 (CD); 650 (CCD); 410 (RD); 10 (AS); < 7 (EC)	
Catalyst plant: production sector (84), quality control (17), internal controls (21), external controls (25)	Mean Pd concentrations in PM_{10}—area sampling: 0.05 (SSD); 0.17 (CD); 4.05 (PCD); 7.70 (RS); 0.35 (RFD); 0.04 (remaining sectors: AL, AS); $<0.02 \times 10^{-3}$ (EC) μg/m^3	Blood: 950 ± 610 (SSD); 1020 ± 820 (CD); 1030 ± 790 (PCD); 2020 ± 1230 (RS); 850 ± 490 (RFD); 880 ± 330 (AL); 890 ± 670 (AS); 50 ± 20 (EC)	Violante et al. (2005)
	Personal sampling: 0.12, 0.03, 1.44, 5.75, 0.56, 0.03 μg/m^3, in the above departments, respectively; N.A. (EC)		

(continued)

Table 2 (continued)

Workers (number)	Environmental exposure	Urine concentrations	References
		Mean (±SD) levels (ng/L, if not indicated otherwise)	
Catalyst plant: production sector (90), quality control (16), internal controls (16), external controls (25)	Mean Pd concentrations in PM_{10}—area sampling: 0.05 ± 0.01 (SSD); 0.17 ± 0.08 (CD); 4.05 ± 2.38 (CCD); 7.70 ± 4.15 (RD); 0.04 ± 0.03 (AD); $< 0.02 \times 10^{-3}$ (EC) $\mu g/m^3$	Blood: 670 ± 450 (SSD); 1020 ± 820 (CD); 1030 ± 790 (CCD); 1310 ± 1040 (RD); 880 ± 330 (Qc); 910 ± 640 (AD); 50 ± 20 (EC)	Cristaudo et al. (2007)
	Personal sampling: 0.12 ± 0.06, 0.03 ± 0.02, 1.76 ± 2.41, 5.75 ± 3.04, 0.03 ± 0.002, $\mu g/m^3$ in the above departments, respectively; N.A. (EC)		
Rhodium			
Catalyst plant: production sectors (12), administrative service (10), external controls (10)	Mean Rh concentrations in PM_{10}—area sampling: 1.0×10^{-3} (SSD); 2.0×10^{-3} (CD); 3.0×10^{-3} (CCD); 1.0×10^{-3} (RD); 1.0×10^{-3} (AS); $<0.006 \times 10^{-3}$ (EC) $\mu g/m^3$	Blood: 110 (SSD); 2940 (CD); 210 (CCD); 150 (RD); 140 (AS); <3 (EC)	Petrucci et al. (2004)
		Serum: 130 (SSD); 1360 (CD); 170 (CCD); 110 (RD); 100 (AS); <2 (EC)	
Catalyst plant: production sector (90), quality control (16), internal controls (16), external controls (25)	Mean Rh concentrations in PM_{10}—area sampling: 1.0×10^{-3} (SSD); 2.0×10^{-3} (CD); 3.0×10^{-3} (CCD); 1.0×10^{-3} (RD); 1.0×10^{-3} (AD); $<0.006 \times 10^{-3}$ (EC) $\mu g/m^3$	Blood: 110 ± 10 (SSD); 290 ± 15 (CD); 90 ± 4 (CCD); 200 ± 10 (RD); 180 ± 11 (QC); 140 ± 9 (AD); 2 ± 1 (EC)	Cristaudo et al. (2007)
	Personal sampling: 1.0×10^{-3}, 35.0×10^{-3}, 3.0×10^{-3}, 1.0×10^{-3}, 0.1×10^{-3}, $\mu g/m^3$ in the above departments, respectively, N.A. (EC)		
Iridium			
Catalyst plant: production sectors (12), administrative service (10), external controls (10)	Mean Ir concentrations in PM_{10}—area sampling: 2.0×10^{-3} (SSD); 0.6×10^{-4} (CD); 0.07×10^{-3} (CCD); 0.09×10^{-3} (RD); 0.05×10^{-3} (AS); $<0.006 \times 10^{-3}$ (EC) $\mu g/m^3$	Blood: 20 (SSD); 2050 (CD); 30 (CCD); 150 (RD); 40 (AS); 1 (EC)	Petrucci et al. (2004)
		Serum: 20 (SSD); 740 (CD); 30 (CCD); 160 (RD); 20 (AS).; 1 (EC)	

(continued)

Table 2 (continued)

Workers (number)	Environmental exposure	Urine concentrations	References
		Mean (±SD) levels (ng/L, if not indicated otherwise)	
Catalyst plant: production sector (90), quality control (16), internal controls (16), external controls (25)	Mean Ir concentrations in PM_{10}—area sampling: 2.0×10^{-3} (SSD); 0.6×10^{-3} (CD); 0.07×10^{-3} (CCD); 0.09×10^{-3} (RD); 0.05×10^{-3} (AD); $<0.006 \times 10^{-3}$ (EC) μg/m^3	Blood: 20 ± 10 (SSD); 210 ± 15 (CD); 30 ± 2 (CCD); 160 ± 10 (RD); 50 ± 3 (QC); 40 ± 2 (AD); 1 ± 0.8 (EC)	Cristaudo et al. (2007)
	Personal sampling: 2.0×10^{-3}, 0.2×10^{-3}, 0.8×10^{-3}, 1.0×10^{-3}, 0.06×10^{-3} μg/m^3 in the above departments, respectively; N.A. (EC)		

AD administrative department; *AL* analytical laboratory; *AS* administrative service; *CCD* chemical catalyst department; *CD* coating department; *EC* external controls; *MS* mechanical section; *PCD* process catalyst department; *PS* production section; *PM* particulate matter; *RFD* refinery department; *RD* recycling department; *RS* recycling service; *SD* standard deviation; *SSD* salt and solution department; *TSP* total suspended particles group of researchers (Messerschmidt et al. 1992) reported a significantly higher mean Pt level in the urine of occupationally exposed subjects compared to controls. A clear correlation between blood and urine Pt levels was reported by Farago et al. (1998) in occupationally-exposed precious metal workers. In this group, the mean urinary Pt level was higher than those measured in motorway maintenance workers and non-exposed controls. As mentioned previously, these latter concentrations were affected by Pt background exposure levels due to working on a motorway or living in an urban area with high traffic. Pt concentrations in urine samples from workers of a Pt refinery and catalyst production company were measured and stratified according to the level of occupational exposure e.g. (i) currently high, (ii) previously high, (iii) currently low and (iv) no exposure (Schierl et al. 1998). The authors demonstrated that urinary excretion of Pt from currently high-exposed workers was about 1,000-fold higher than that of non-exposed controls. Interestingly, they found that four persons who had ceased working in the Pt industry 2–6 years previously on account of Pt allergy, although asymptomatic at the time of biological monitoring, still excreted 25-fold more Pt than the control group. These data suggest that following occupational exposure, there may be a long-lasting Pt pool in the body that is responsible for a slow and long-term release of the metal in urine. Pt excretion from subjects who had had little contact with Pt salts was similar to that of controls. However, when two volunteers were exposed to Pt dust for 4 h while performing filtration and hand crushing procedures in a refinery, urinary Pt excretion reached the maximum level nearly 10 h after inhalative exposure and then followed an exponential decay with a half-life of about 50 h. As confirmation of the association between urinary Pt concentrations and different exposure levels, Petrucci et al. (2004, 2005) and Cristaudo et al. (2007) reported great variability in mean data for urine Pt content in relation to work sites in a catalyst plant. The good correlation with airborne metal concentrations makes urinary Pt an efficient biological marker of occupational exposure.

Concerning occupational exposure to vehicle traffic, Schierl (2000) reported a mean concentration of urinary Pt levels of 6.5 ng/g creatinine in subjects who took part in different studies but were not involved in the Pt catalyst industry. Among the latter group, bus and taxi drivers had median Pt levels of 2.8 and 1.3 ng/L, while Pt concentrations in road construction workers ranged from 0.1 to 4.4 ng/L (Begerow and Dunemann 2000). Compared to catalyst industry workers with Pt excretion of up to 6,000 ng/g creatinine (Schierl et al. 1998), concentrations due to environmental exposure were rather small, although extremely important for the evaluation of low level exposure risks. Subsequent investigations were performed to determine urine Pt concentrations in subjects occupationally-exposed to urban air with heavy traffic, but results were inconsistent (Iavicoli et al. 2004, 2007; Óvári et al. 2007). In keeping with findings from Schierl (2000), comparable levels were observed respectively in urine samples from traffic police officers and tram drivers working in the city of Rome, Italy (Iavicoli et al. 2004, 2007). In the study carried out by Iavicoli et al. (2004), no significant differences in Pt urinary levels were observed when control and exposed subjects were compared at the beginning and end of the work shift. Moreover, no significant differences in urinary Pt concentrations were found in the two study groups at the same time points. This suggests that urinary Pt concentrations may be influenced by comparable environmental living conditions and dietary habits that result in a similar overall exposure to the metal. The absence of statistically significant variations in the urinary Pt concentrations at the beginning and end of the work shift may also be explained by assuming a Pt half-life far longer than the duration of the work shift, as previously reported by Schierl et al. (1998). Nevertheless, the study carried out on Italian tram drivers did reveal a significant difference in Pt levels between exposed and control subjects (Iavicoli et al. 2007), although these results were considerably lower than those determined by Óvári et al. (2007). In this study (Óvári et al. 2007), performed in Vienna (Austria) and Budapest (Hungary), tram drivers working on tram routes with high automotive traffic density were chosen for urinary sampling and Pt levels were compared with data available for the general population (Zaray et al. 2004). Tram drivers were found to have significantly higher mean urinary Pt concentrations than non-exposed subjects (Óvári et al. 2007). Interestingly, significant increases were reported in urinary Pt concentrations measured after the shift. However, these biological monitoring results may have been influenced by a number of conditions such as the different indoor and outdoor PGE exposure levels, car traffic density in the work areas, the different city tramway networks and the types of tramcars (with or without ventilation systems). All these aspects should be taken into consideration when evaluating biomonitoring results reported for workers exposed to vehicle traffic.

2.2.2 Palladium

The analysis of urine samples obtained from workers engaged in a catalyst plant revealed a significant correlation between urine Pd levels and airborne Pd concentrations, indicating that urine could be used as a suitable matrix for evaluating short-term Pd exposure in this occupational setting (Petrucci et al. 2004; Violante et al. 2005; Cristaudo et al. 2007) (Table 2). The highest mean urine values were detected in the production of catalyst and in chemical catalyst departments where researchers observed the highest concentrations of soluble Pd. This interesting finding seems to suggest that Pd solubility is an extremely important factor that influences its toxicokinetic behaviour and the metal content in urine samples. In fact, as reported by Cristaudo et al. (2007), the chemical catalyst department, where Pd salts were handled, showed a lower airborne Pd concentration (4.05 $\mu g/m^3$) as compared with the highest level found in the recycling department (7.07 $\mu g/m^3$). However, it was the sector in which the highest soluble Pd fraction (63.3 %) was recovered. In the recycling department, where all PGEs were used in the metallic form, this fraction was only 7.0 %.

In subjects occupationally-exposed to automotive traffic, no measurable increase in urinary Pd excretion was observed when compared with controls (Begerow and Dunemann 2000; Iavicoli et al. 2007) (Table 2). In fact Iavicoli et al. (2007) did not find significant differences between mean urinary Pd levels in Rome tram drivers and non-exposed controls. Unlike the findings for Pt and Rh, urinary Pd levels did not appear to be affected by prolonged exposure to urban airborne Pd. Begerow and Dunemann (2000) had previously reported similar results for road construction workers who did not manifest significantly different urinary Pd concentrations compared to the school leaver control group. Nevertheless, ranges and mean values observed by Iavicoli et al. (2007) were slightly lower than those reported by Begerow and Dunemann (2000). This might have been due to the fact that external exposure is more limited in tram drivers than in road construction workers, since their working activity is performed exclusively inside the public transport vehicle.

2.2.3 Rhodium

It has been demonstrated that urinary Rh biomonitoring results of workers in catalyst plants are consistent with the level of environmental exposure (Petrucci et al. 2004; Cristaudo et al. 2007). In accordance with measurements reported by Petrucci et al. (2004), Cristaudo et al. (2007) found the highest mean Rh concentration in samples collected from workers employed in the catalyst department where the highest personal environmental exposure to this metal was detected.

The values reported in this study (Cristaudo et al. 2007) were greater than those detected in urine samples collected from workers exposed to traffic, although these were significantly different compared to those of controls (Iavicoli et al. 2007) (Table 2).

2.2.4 Iridium

Kiilunen et al. (2004) analyzed the Ir content in urine from Finnish workers engaged in refining noble metals, manufacturing catalysts and repairing car exhaust systems. The highest mean concentration was measured in the department where car catalysts were manufactured. Ir levels measured in urine samples collected from subjects employed in an industrial production and recycling PGE plant showed comparable values in all the investigated departments (Petrucci et al. 2004; Cristaudo et al. 2007) without significant differences with external controls (Cristaudo et al. 2007) (Table 2).

Urinary Ir content was also measured in a population of Rome tram drivers occupationally-exposed to traffic (Iavicoli et al. 2008a). Mean Ir values did not show significant differences between exposed workers and controls. Interestingly, these results suggest that tram drivers who are occupationally-exposed to vehicle traffic, do not incorporate more Ir than the general population living in an urban environment.

2.3 *Other Matrices*

Hair is generally considered to be a storage tissue for several metals (Batista et al. 1996; Schuhmacher et al. 1996). PGE levels in the hair of exposed workers were shown to be significantly higher than in controls and extremely sensitive to the different levels of exposure found in workplace areas (Petrucci et al. 2004, 2005; Violante et al. 2005; Cristaudo et al. 2007). Pt values ranged from 40 to 2550 ng/g in the study performed by Petrucci et al. (2004) and 80 ± 60–2260 ± 1590 ng/g in two other investigations on PGE hair concentrations (Petrucci et al. 2005; Cristaudo et al. 2007). Violante et al. (2005) observed Pd concentrations ranging from 140 ± 80 to 5540 ± 2780 ng/kg in the administrative and refining departments of a catalyst plant. In the same sectors, Pd values ranging from 90–5180 and 140 ± 60–4720 ± 2600 ng/g were reported by Petrucci et al. (2004) and Cristaudo et al. (2007), respectively. These results were in accordance with environmental levels of the metal in the different areas of the plant. In the same catalyst plant, concentrations ranging from 20 ± 1 to 310 ± 20 and 0.1 ± 1 to 200 ± 11 ng/g were reported for Rh and Ir respectively (Petrucci et al. 2004; Cristaudo et al. 2007). This unexpected finding was probably due to the large amounts of exogenous metal absorbed on the outer surface of hair, and which are difficult to remove by washing. Thus, external contamination of hair interferes with the accurate determination of PGE contained within the hair strands, which makes this tissue less than desirable for use as a biomarker of long-term exposure (Petrucci et al. 2005). In fact, PGE levels in hair are much less affected by the duration of exposure—that is, by the number of years spent in the same plant, especially in cases where pollution is very high. In conditions of heavy exposure, hair tissue acts as an environmental filter retaining PGE dust on its surface. This is confirmed by the very strong association between PGE hair levels and PGE concentrations in airborne matter collected from the same subjects by means of personal devices (Cristaudo et al. 2007).

3 Biomarkers of Effect

The most significant health effect caused by exposure to soluble PGE compounds is sensitization. Pt salts have been reported to induce hypersensitivity reactions with respiratory symptoms such as rhinitis, conjunctivitis, asthma, contact urticaria and occasionally contact dermatitis (Merget et al. 1988; Niezborala and Garnier 1996; Cristaudo et al. 2005). Pt sensitization is generally considered to occur through an IgE mediated reaction (Biagini et al. 1985; Murdoch et al. 1986). This explains why skin-prick testing, such as the insertion of a needle previously passed through a drop of a tested compound into the epidermal surface of the forearm, can be used for its detection, both for surveillance purposes and in the clinical diagnosis of Pt-induced hypersensitivity disorders (Baker et al. 1990; Brooks et al. 1990; Merget et al. 1991; Santucci et al. 2000; Cristaudo et al. 2005, 2007). Positive reactions to patch test examinations for Pt salts in symptomatic exposed workers, such as local allergic reactions on small areas of the back where the diluted chemicals were planted, may also indicate delayed hypersensitivity as a possible mechanism of Pt action (Cristaudo et al. 2005; Santucci et al. 2000). Cases of occupational rhinocongiuntivitis and asthma, as well as contact dermatitis have been described in workers exposed to Pd (Rebandel and Rudzki 1990; Daenen et al. 1999; Santucci et al. 2000; Kielhorn et al. 2002). Sensitization to Pd salts has been reported in skin prick tests (Daenen et al. 1999; Murdoch et al. 1986; Murdoch and Pepys 1987) and patch tests (Santucci et al. 2000; Cristaudo et al. 2005). Similarly, occupational allergic contact dermatitis, urticaria and asthma have been diagnosed in subjects working in the jewelry trade (Bedello et al. 1987; de la Cuadra and Grau-Massanés 1991; Merget et al. 2010) and in the fields of refinery and catalyst production where workers are exposed to Rh (Murdoch et al. 1986; Murdoch and Pepys 1987; Santucci et al. 2000; Cristaudo et al. 2005, 2007; Goossen et al. 2011). In the workplace, cases of sensitization to Ir are known but rare (IUPAC 2004). Contact urticaria and respiratory symptoms have been reported in workers exposed to Ir salts and positive at prick tests (Bergman, et al. 1995; Santucci et al. 2000; Cristaudo et al. 2005).

In this scenario, it is quite challenging to identify biomarkers of an early effect, i.e. a measurable biochemical, structural, functional, behavioral or other kind of alteration in an organism indicating a subclinical effect or even an early, reversible clinical response. At present, there are no biomarkers able to meet these criteria and be practically employed for occupational biological monitoring. However, there are some interesting findings that can be extrapolated from in vitro and in vivo studies for further discussion and investigation.

The latency period between initial exposure to Pt compounds and the appearance of the first symptoms of hypersensitivity ranges from 1 week to more than 20 years, but sensitization usually develops within a period ranging from a few months to a few years (SCOEL 2011; Hughes 1980; Merget et al. 1988, 1991; Pepys et al. 1979). Therefore, potential early effect biomarkers should be able to detect preclinical biological alterations occurring in this latency “window”. In connection with this, Merget et al. (1995), investigating the most sensitive indicators of early occupational asthma due to Pt salts, demonstrated that the sequence of parameters that triggered the disease was: skin sensitization, symptoms (e.g. rhinitis and shortness of breath) and bronchial hyperresponsiveness.

The presence of Pt salt-specific IgE antibodies and unusually high levels of total IgE in serum was reported in exposed workers (Biagini et al. 1985; Bolm-Audorff et al. 1992; Brooks et al. 1990; Cromwell et al. 1979; Merget et al. 1988; Murdoch et al. 1986; Murdoch and Pepys 1987). Out of 306 Pt refinery workers, 38 had a positive skin prick test to Pt salts (Murdoch et al. 1986). Total and specific IgE levels were higher in 63 and 62 % Pt salt prick test positive workers compared with only 16 and 6 % prick test negative group, respectively. Subjects who reported work-related symptoms of respiratory allergy following exposure to Pt salts in a chemical industry had significantly more positive skin prick tests and higher total IgE as well as Pt specific IgE levels compared to the other workers (Bolm-Audorff et al. 1992). Interestingly, Merget et al. (1995) demonstrated that, at the time of skin test conversion, 2 out of 8 converter operators manifested a marked increase in total IgE. Likewise, catalyst production workers who showed conversion at the skin prick test for Pt salt, during a 5-year surveillance period, had higher levels of total IgE compared to controls (Merget et al. 2001). A strong association between total IgE levels and sensitization was also detected by Calverley et al. (1999). Moreover, in this study (Calverley et al. 1999), subjects who had worked for longer periods before sensitization, showed a tendency for gradual, serial increase in IgE. Therefore, alterations in total and specific IgE levels, as well as a gradual increase in these parameters over an extended period of occupational medical surveillance should be given careful consideration and validated as possible early markers of hypersensitivity effects.

Other approaches that might identify occupational and environmental exposure to PGEs leading to immunological changes include cytokine profiling and the measurement of lymphocyte subpopulations defined by the expression of specific surface markers (Schwenk et al. 2008; Orfao and Ruiz-Arguelles 1996). Regarding cytokine release, interesting data can be extrapolated from in vitro (Di Gioacchino et al. 2004; Boscolo et al. 2004) and in vivo studies (Iavicoli et al. 2006, 2008b, 2010, 2012) demonstrating the ability of PGE compounds to influence T helper-1 (Th-1) and Th-2 cytokine synthesis. A clear inhibition of the in vitro release of tumor necrosis factor (TNF)-α, interferon (IFN)-γ, and interleukin (IL)-5 was observed in peripheral blood mononuclear cells (PBMCs) exposed to different concentrations of chlorinated ammonium Pt compounds, confirming the immunotoxic role of Pt salts (Di Gioacchino et al. 2004). The inhibitory role of Pt, Pd and Rh salts on the production of these cytokines in PBMCs was subsequently reported by the same group of researchers (Boscolo et al. 2004). Interestingly, they found that Pd compounds were more immunotoxic than Pt and Rh salts. PGE immunotoxicity was clearly dependent on the metal salt speciation (Di Gioacchino et al. 2007). A modulatory effect on the immune system was also demonstrated when PBMCs collected from Pd-sensitized (Reale et al. 2011) and non-sensitized women (Boscolo et al. 2010) were exposed to this metal in nanoparticulate form. In fact lipopolysaccharide-stimulated PBMCs from non-sensitized women showed enhanced INF-γ release, while a decreased production of TNF-α was detected when both PBMCs from sensitized and non- sensitized women were exposed to Pd-nanoparticles.

In vivo results also demonstrated the ability of Pd (Iavicoli et al. 2006, 2008b), Ir (Iavicoli et al. 2010) and Rh (Iavicoli et al. 2012) to exert an immuno-modulating effect after oral exposure. Treatment with Pd salt induced alterations in the Th-1/Th-2 cytokine balance, as demonstrated by increased levels of IL-4 after subacute exposure (Iavicoli et al. 2006) and enhanced INF-γ production as well as a J-shaped IL-2 dose-response following subchronic treatment (Iavicoli et al. 2008b). Similarly, Ir was able to induce a skewing toward a Th-2 immune response in rats, with a dose-dependent increase in IL-4 and a decrease in IL-2 and INF-γ serum levels after subacute exposure (Iavicoli et al. 2010). More recently, a clear inhibition in cytokine release was detected by Iavicoli et al. (2012) in rats sub-acutely treated with increasing concentrations of an Rh salt.

To measure lymphocyte subpopulations, Raulf-Heimsoth et al. (2000) examined the T-cell receptor (TCR) repertoire distribution in PBMCs collected from catalyst and refinery plant workers who had occupational asthma and a positive skin prick test for sodium hexachloroplatinate. Moreover, the authors also assessed in vitro the TCR in T-cells after stimulation with this Pt salt. The frequency of CD3-positive lymphocytes in sensitized workers was significantly higher for Vα2a-, Vβ11 and Vβ21.3 positive T-cells than in controls. The number of Vβ5.3, Vβ6.7, Vβ8a/Vβ8, Vβ13.1, Vβ20 and Vβ21.3-positive CD3 cells was dose-dependently enhanced in Pt salt cultures compared to non-stimulated controls. The relationship observed between Vβ expression, allergen exposure and sensitization, respectively, emphasized the importance of allergen exposure in transiently shaping the T-cell repertoire. Results suggested that selective expansion or accumulation of certain CD3-positive T-cell subsets occurred in the blood of patients with Pt salt-sensitization but not in the non-exposed control group. The mechanism by which Pt salt may activate T-cells is not clear. It has been hypothesized that Pt salt may bind to different self peptides which are recognized as foreign when presented by class II major histocompatibility complex molecules. It is also possible that Pt salt acts as a superantigen in the human PBMC system. Further investigation is needed to establish whether a particular TCR repertoire is a useful biomarker or a possible risk factor for the development of Pt salt sensitization. For this purpose it would also be interesting to examine the TCR repertoire in non-sensitized Pt-exposed workers.

Recent in vivo studies have demonstrated the toxic action of Rh and Ir on the renal function of animals sub-acutely or sub-chronically treated via the oral route (Iavicoli et al. 2011, in press). This was ascertained by analysing alterations in the levels of low-molecular weight proteins, such as retinol binding protein and β2-microglobulin, and high-molecular weight albumin in urine samples of rats exposed to increasing doses of PGE salts. Findings suggest that these biomarkers could be indicators of early effect, however, further investigation and validation are needed before they can be used in occupational settings.

Genotoxicity biomarkers are another type of biomarker of effect. These biomarkers are used to measure the specific effects of occupational and environmental exposure, to predict the risk of disease or monitor the effectiveness of exposure control procedures in subjects exposed to genotoxic chemicals (Manno et al. 2010). The genotoxicity of Pt and Pd compounds has been investigated using the cytokinesis block micronucleus test in human PBMCs (Gebel et al. 1997). Pt (IV) chloride ($PtCl_4$) was found to be significantly genotoxic, while neither the divalent compound K_2PtCl_6 nor the divalent $PtCl_2$ revealed any micronucleus inducing activity in PBMCs. None of the Pd compounds tested had any significant effect on the number of micronuclei in investigated cells. These findings may be due to the fact that non-genotoxic Pt and Pd compounds can be easily degraded, substituted or hydrolised, so that they do not maintain their structural integrity long enough to reach and react with cellular DNA. A significant induction of micronuclei was observed in lymphocytes treated with Pt compounds such as $(NH_4)_2PtCl_4$, $PtCl_4$, Pt(II) chloride ($PtCl_2$), and Rh (III) chloride

($RhCl_3$) compared with controls (Migliore et al. 2002). In agreement with data reported by Gebel et al. (1997), $PtCl_4$ showed a significant micronucleus induction while, $(NH_4)_2PtCl_4$ and $PtCl_2$ appeared to be weaker genotoxic inducers. In tests using $RhCl_3$ and Pd salts such as $(NH_4)_2PdCl_4$ and PdCl, a significant increase in micronucleus frequency was observed only at higher exposure doses. Findings for the comet assay revealed oxidative DNA damage for $PtCl_4$ and $RhCl_3$. None of the other metal compounds investigated induced this effect. Current knowledge on metal genotoxicity mechanisms suggests that the genotoxic potential of all these diverse metals and their compounds does not depend on a single mechanism. Two main actions seem to be involved: the enhanced formation of radical oxygen species that leads to lipid peroxidation and DNA damage, and interference with DNA repair and/or DNA replication processes (Migliore et al. 2002).

4 Biomarkers of Susceptibility

A biomarker of susceptibility is defined as an indicator of the inherent or acquired ability of an organism to respond to the exposure to a chemical (Manno et al. 2010). Since the development of sensitization to inhaled allergens is caused by the interaction of numerous genetic and environmental factors, Newman Taylor et al. (1999) examined the possible role of the HLA phenotype in developing an IgE-mediated sensitization to ammonium hexacloroplatinate. HLA typing in 44 sensitized employees of a refinery plant and in 57 non-sensitized controls was therefore performed (Newman Taylor et al. 1999). Compared with controls matched for intensity, duration of exposure and ethnic background, they found an excess of HLA-DR3 and a deficit of HLA-DR6 in cases with a skin test response to ammonium hexacloroplatinate. The chances of a case being HLA-DR3 positive or HLA-DR6 negative were far greater in the "low" exposure groups compared to the "high" ones (Newman Taylor et al. 1999). These results suggest that in individuals occupationally-exposed to ammonium hexacloroplatinate, genetic susceptibility is an important determinant of sensitization. Although the absolute risk of sensitization was higher in more heavily exposed subjects, in those who were HLA-DR3 positive or DR6 negative the relative risk of getting sensitized to ammonium hexacloroplatinate was greater in workers who were less heavily exposed (Newman Taylor 2001). Clearly, genetic polymorphism may be a risk factor that contributes to individual susceptibility to the emergence of sensitization.

5 Discussion and Conclusions

Increased Pt, Pd and Rh concentrations in blood and serum in exposed workers compared to non-exposed controls have been shown to be suitable biological markers of exposure in industrial settings. Generally, these values closely resemble environmental levels of exposure as has been demonstrated by the positive relationship between blood and serum Pt, Pd and Rh levels and their airborne concentrations collected by means of either area or individual samplers (Petrucci et al. 2004, 2005; Violante et al. 2005; Cristaudo et al. 2007). In fact, the highest levels of these PGEs were found in workers employed in the departments where the highest airborne concentrations were measured. On the other hand, blood and serum Ir levels did not closely reflect environmental concentrations. This suggests that Ir concentrations in these media are influenced by other workplace or individual factors, and it is therefore important to perform an adequate biological monitoring analysis to assess the real exposure of workers.

Interestingly, detectable PGE levels were reported in non-occupationally exposed subjects. These findings may be related to increased PGE concentrations in the general living environment as well as to possible contamination due to metal release from dental prostheses (Merget et al. 2002; Iavicoli et al. 2004). In this context, future research should aim to provide more information on blood/serum PGE levels in workers exposed to low levels of these metals such as in the case of exposure to vehicle traffic emissions. This step is essential in order to obtain a complete understanding of exposure levels in different occupational scenarios so that a suitable risk assessment and management can be devised to protect the health of workers even in conditions of low exposure.

Compared to non-exposed controls, a clear difference was noted in urinary Pt and Rh levels both in workers exposed in catalyst plants and those exposed to vehicle traffic. Generally, these urinary PGE levels closely reflected their environmental concentrations, thus providing good information on the current degree of occupational exposure. This was demonstrated also by the great variability in mean urinary levels in response to airborne concentrations found in different departments of the plant (Petrucci et al. 2005; Cristaudo et al. 2007). Interestingly, outdoor workers exposed to vehicle traffic emissions had lower PGE concentrations compared to subjects employed in the production and recycling catalyst plant (Iavicoli et al. 2004, 2007; Óvári et al. 2007; Schierl et al. 2000). This may have been due to airborne PGE concentrations that were higher in indoor industrial settings than in the general environment (i.e. Cristaudo et al. 2007; Iavicoli et al. 2008c). Moreover, factors such as physical stress at work, climate and microclimate, intensity of work production/activities, job location and number of daily working hours, as well as traffic density (especially for traffic police officers and tram-drivers) may all influence respiratory adsorption of these metals and the internal doses detected.

Concerning Pd, urinary levels closely resembled industrial exposure, although controversy remains over the possibility of using these biomarkers in workers exposed to vehicle traffic emissions (Begerow and Dunemann 2000; Iavicoli et al. 2007). As regards Ir, no significant increase was found in urine samples of occupationally-exposed subjects, although the limited number of studies available in the literature does not allow us to reach definite conclusions on the role of Ir as a suitable biomarker of exposure (Cristaudo et al. 2007; Iavicoli et al. 2008a; Kiilunen et al. 2004).

All these findings indicate that, even if PGEs have similar physico-chemical properties, they may react differently with biological systems, possibly on account of diverse metal speciation, solubility, interactions with other occupational pollutants or general external and individual exposure conditions. For this reason, it is important to gain a deeper understanding of the toxicokinetic behaviour of PGEs. By determining exposure and adsorption routes and metabolism and elimination pathways, it will be possible to define new potential biomarkers of exposure and effective dose and understand possible confounding factors.

With regard to biomarkers of effect, no indicators able to reveal early adverse health conditions and easy to use in occupational health practice are currently available. However, considering the IgE-mediated hypersensitivity reactions induced by PGE salts, the measurement of salt-specific IgE levels and the total content of IgE antibodies in serum could be included among possible biomarkers of effect. These biomarkers may be able to identify alterations in the immune system in a pre-clinical condition, before the appearance of hypersensitivity symptoms. However, the feasibility of these indicators should be confirmed in future field studies undertaken specifically to define their role in occupational health practice. Data obtained for cytokine profiling and evaluation of the TCR repertoire appear to be extremely promising, although still in a preliminary phase, and therefore research studies should be planned in different occupational settings to confirm the possibility of using these biomarkers in a future health surveillance program. New possibilities in the biological monitoring of PGEs have emerged from recent studies that evaluated the toxicity of Rh and Ir on renal function (Iavicoli et al. 2011, in press). These results provide a stimulus to verify the possible early appearance of biochemical alterations in the renal system functionality of occupationally-exposed populations.

At present, evidence of the genotoxic potential of PGEs is quite limited (Gebel et al. 1997; Migliore et al. 2002), although information on this matter is extremely important for occupational risk assessment, and particularly for the evaluation of carcinogenic risks. Therefore, future studies should aim to confirm possible genotoxic PGE action and its underlying mechanisms. However, from an ethical point of view, a balance should be found between the benefit to a worker in terms of preventive action and the possible adverse impact on his/her working condition and/or quality of life, when considering whether to use these biomarkers in workplace biological monitoring (Manno et al. 2010). The same ethical aspects are involved in the use of susceptibility biomarkers, although only preliminary data are currently available on these tools.

In conclusion, biological monitoring is a promising instrument for adequately assessing and managing the risk of PGE exposure in occupational and environmental settings. Occupational biological monitoring of PGEs can currently benefit from suitable exposure biomarkers that have been detected in different biological matrices. Further studies are needed to define indicators of early effect. These should then be confirmed and validated in field studies so that they can be applied in future occupational health practice.

References

Baker DB, Gann PH, Brooks SM, Gallagher J, Bernstein IL (1990) Cross-sectional study of platinum salts sensitization among precious metals refinery workers. Am J Ind Med 18:653–664

Batista J, Schuhmacher M, Domingo JL, Corbella J (1996) Mercury in hair for a child population from Tarragona Province, Spain. Sci Total Environ 193:143–148

Bedello PG, Goitre M, Roncarolo G, Bundino S, Cane D (1987) Contact dermatitis to rhodium. Contact Dermatitis 17:111–112

Begerow J, Dunemann L (2000) Internal platinum and palladium exposure of the general population with emphasis on the exposure from automobile exhaust and dental restorative alloys. In: Zereini F, Alt F (eds) Anthropogenic platinum-group element emissions. Their impact on man and environment. Springer, Berlin

Bergman A, Svedberg U, Nilsson E (1995) Contact urticaria with anaphylactic reactions caused by occupational exposure to iridium salt. Contact Dermatitis 32:14–17

Biagini RE, Bernstein IL, Gallagher JS, Moorman WJ, Brooks S, Gann PH (1985) The diversity of reaginic immune responses to platinum and palladium metallic salts. J Allergy Clin Immunol 76:794–802

Bolm-Audorff U, Bienfait HG, Burkhard J, Bury AH, Merget R, Pressel G, Schultze-Werninghaus G (1992) Prevalence of respiratory allergy in a platinum refinery. Int Arch Occup Environ Health 64:257–260

Boscolo P, Di Giampaolo L, Reale M, Castellani ML, Ritavolpe A, Carmignani M, Ponti J, Paganelli R, Sabbioni E, Conti P, Di Gioacchino M (2004) Different effects of platinum, palladium, and rhodium salts on lymphocyte proliferation and cytokine release. Ann Clin Lab Sci 34:299–306

Boscolo P, Bellante V, Leopold K, Maier M, Di Giampaolo L, Antonucci A, Iavicoli I, Tobia L, Paoletti A, Montalti M, Petrarca C, Qiao N, Sabbioni E, Di Gioacchino M (2010) Effects of palladium nanoparticles on the cytokine release from peripheral blood mononuclear cells of non-atopic women. J Biol Regul Homeost Agents 24:207–214

Brooks SM, Baker DB, Gann PH, Jarabek AM, Hertzberg V, Gallagher J, Biagini RE, Bernstein IL (1990) Cold air challenge and platinum skin reactivity in platinum refinery workers. Bronchial reactivity precedes skin prick response. Chest 97:1401–1407

Calverley AE, Rees D, Dowdeswell RJ (1999) Allergy to complex salts of platinum in refinery workers: prospective evaluations of IgE and Phadiatop status. Clin Exp Allergy 29:703–711

Cristaudo A, Picardo M, Petrucci F, Forte G, Violante N, Senofonte O, Alimonti A, Sera F (2007) Clinical and allergological biomonitoring of occupational hypersensitivity to platinum group elements. Anal Lett 40:3343–3359

Cristaudo A, Sera F, Severino V, De Rocco M, Di Lella E, Picardo M (2005) Occupational hypersensitivity to metal salts, including platinum, in the secondary industry. Allergy 60:159–164

Cromwell O, Pepys J, Parish WE, Hughes EG (1979) Specific IgE antibodies to platinum salts in sensitized workers. Clin Allergy 9:109–117

Daenen M, Rogiers P, Van de Walle C, Rochette F, Demedts M, Nemery B (1999) Occupational asthma caused by palladium. Eur Respir J 13:213–216

de la Cuadra J, Grau-Massanés M (1991) Occupational contact dermatitis from rhodium and cobalt. Contact Dermatitis 25:182–184

Di Gioacchino M, Di Giampaolo L, Verna N, Reale M, Di Sciascio MB, Volpe AR, Carmignani M, Ponti J, Paganelli R, Sabbioni E, Boscolo P (2004) In vitro effects of platinum compounds on lymphocyte proliferation and cytokine release. Ann Clin Lab Sci 34:195–202

Di Gioacchino M, Verna N, Di Giampaolo L, Di Claudio F, Turi MC, Perrone A, Petrarca C, Mariani-Costantini R, Sabbioni E, Boscolo P (2007) Immunotoxicity and sensitizing capacity of metal compounds depend on speciation. Int J Immunopathol Pharmacol 20(2 Suppl 2):15–22

Djingova R, Kovacheva P, Wagner G, Markert B (2003) Distribution of platinum group elements and other traffic related elements among different plants along some highways in Germany. Sci Total Environ 308:235–246

Ek KH, Rauch S, Morrison GM, Lindberg P (2004) Platinum group elements in raptor eggs, faeces, blood, liver and kidney. Sci Total Environ 334–335:149–159

Farago ME, Kavanagh P, Blanks R, Kelly J, Kazantzis G, Thornton I, Simpson PR, Cook JM, Delves HT, Hall GE (1998) Platinum concentrations in urban road dust and soil, and in blood and urine in the United Kingdom. Analyst 123:451–454

Gebel T, Lantzsch H, Plessow K, Dunkelberg H (1997) Genotoxicity of platinum and palladium compounds in human and bacterial cells. Mutat Res 389:183–190

Gómez B, Palacios MA, Gómez M, Sanchez JL, Morrison G, Rauch S, McLeod C, Ma R, Caroli S, Alimonti A, Petrucci E, Bocca B, Schramel P, Zischka M, Petterson C, Wass U (2002) Levels and risk assessment for humans and ecosystems of platinum-group elements in the airborne particles and road dust of some European cities. Sci Total Environ 299:1–19

Goossens A, Cattaert N, Nemery B, Boey L, De Graef E (2011) Occupational allergic contact dermatitis caused by rhodium solutions. Contact Dermatitis 64:158–161

Hooda PS, Miller A, Edwards AC (2007) The distribution of automobile catalysts-cast platinum, palladium and rhodium in soils adjacent to roads and their uptake by grass. Sci Total Environ 384:384–392

Hooda PS, Miller A, Edwards AC (2008) The plant availability of auto-cast platinum group elements. Environ Geochem Health 30:135–139

Hughes EG (1980) Medical surveillance of platinum refinery workers. J Soc Occup Med 30:27–30

Iavicoli I, Bocca B, Carelli G, Caroli S, Caimi S, Alimonti A, Fontana L (2007) Biomonitoring of tram drivers exposed to airborne platinum, rhodium and palladium. Int Arch Occup Environ Health 81:109–114

Iavicoli I, Bocca B, Caroli S, Caimi S, Alimonti A, Carelli G, Fontana L (2008a) Exposure of Rome city tram drivers to airborne platinum, rhodium, and palladium. J Occup Environ Med 50:1158–1166

Iavicoli I, Bocca B, Petrucci F, Senofonte O, Carelli G, Alimonti A, Caroli S (2004) Biomonitoring of traffic police officers exposed to airborne platinum. Occup Environ Med 61:636–639

Iavicoli I, Carelli G, Bocca B, Caimi S, Fontana L, Alimonti A (2008b) Environmental and biological monitoring of iridium in the city of Rome. Chemosphere 71:568–573

Iavicoli I, Carelli G, Marinaccio A, Fontana L, Calabrese E (2008c) Effects of sub-chronic exposure to palladium (as potassium hexachloro-palladate) on cytokines in male Wistar rats. Hum Exp Toxicol 27:493–497

Iavicoli I, Carelli G, Marinaccio A, Magrini A, Fontana L, Boscolo P, Bergamaschi A (2006) The effects of sub-acute exposure to palladium on cytokines in male Wistar rats. Int J Immunopathol Pharmacol 19(4 Suppl):21–24

Iavicoli I, Fontana L, Marinaccio A, Alimonti A, Pino A, Bergamaschi A, Calabrese EJ (2011) The effects of iridium on the renal function of female Wistar rats. Ecotoxicol Environ Saf 74:1795–1799

Iavicoli I, Fontana L, Marinaccio A, Bergamaschi A, Calabrese EJ (2010) Iridium alters immune balance between T helper 1 and T helper 2 responses. Hum Exp Toxicol 29:213–219

Iavicoli I, Sgambato A, Fontana L, Marinaccio A, Leso V, Corbi M, Bergamaschi A, Calabrese EJ (2012) Effects of sub-acute exposure to rhodium (as Rh (III) chloride hydrate) on cytokines in female Wistar rats. Bull Environ Contam Toxicol 89:686–692

Iavicoli I, Leso V, Fontana L, Marinaccio A, Bergamaschi A, Calabrese EJ (in press) The effects of rhodium on the renal function of female Wistar rats. Chemosphere. doi:10.1016/j.chemosphere.2013.10.077

International Union of Pure and Applied Chemistry (IUPAC) (2004) Mechanisms of immunosensitization to metals (IUPAC Technical Report). Pure Appl Chem 76:1255–1268

Jarvis KE, Parry SJ, Piper JM (2001) Temporal and spatial studies of autocatalyst-derived platinum, rhodium, and palladium and selected vehicle-derived trace elements in the environment. Environ Sci Technol 35:1031–1036

Johnson Matthey Publications (2013) Platinum 2013 Interim Review. http://www.platinum.matthey.com/media/1631235/platinum_2013_interim_review.pdf. Accessed on 29 November 2013

Kielhorn J, Melber C, Keller D, Mangelsdorf I (2002) Palladium—a review of exposure and effects to human health. Int J Hyg Environ Health 205:417–432

Kiilunen M, Vanhala E, Tossavainen A (2004) Occupational exposure to platinum group metals in Finland. Tox Appl Pharm 197:326–326

Manno M, Viau C; in collaboration with, Cocker J, Colosio C, Lowry L, Mutti A, Nordberg M, Wang S (2010) Biomonitoring for occupational health risk assessment (BOHRA). Toxicol Lett 192: 3–16

Marcheselli M, Sala L, Mauri M (2010) Bioaccumulation of PGEs and other traffic-related metals in populations of the small mammal Apodemus sylvaticus. Chemosphere 80:1247–1254

Mathur R, Balaram V, Satyanarayanan M, Sawant SS, Ramesh SL (2011) Anthropogenic platinum, palladium and rhodium concentrations in road dusts from Hyderabad city, India. Environ Earth Sci 62:1085–1098

Merget R, Caspari C, Dierkes-Globisch A, Kulzer R, Breitstadt R, Kniffka A, Degens P, Schultze-Werninghaus G (2001) Effectiveness of a medical surveillance program for the prevention of occupational asthma caused by platinum salts: a nested case-control study. J Allergy Clin Immunol 107:707–712

Merget R, Caspari C, Kulzer R, Breitstadt R, Rueckmann A, Schultz-Werninghaus G (1995) The sequence of symptoms, sensitization and bronchial hyperresponsiveness in early occupational asthma due to platinum salts. Int Arch Allergy Immunol 107:406–407

Merget R, Kulzer R, Dierkes-Globisch A, Breitstadt R, Gebler A, Kniffka A, Artelt S, Koenig HP, Alt F, Vormberg R, Baur X, Schultze-Werninghaus G (2000) Exposure-effect relationship of platinum salt allergy in a catalyst production plant: conclusions from a 5-year prospective cohort study. J Allergy Clin Immunol 105:364–370

Merget R, Kulzer R, Kniffka A, Alt F, Breitstadt R, Bruening T (2002) Platinum concentrations in sera of catalyst production workers are not predictive of platinum salt allergy. Int J Hyg Environ Health 205:347–351

Merget R, Sander I, van Kampen V, Raulf-Heimsoth M, Ulmer HM, Kulzer R, Bruening T (2010) Occupational immediate-type asthma and rhinitis due to rhodium salts. Am J Ind Med 53:42–46

Merget R, Schultze-Werninghaus G, Bode F, Bergmann EM, Zachgo W, Meier-Sydow J (1991) Quantitative skin prick and bronchial provocation tests with platinum salt. Br J Ind Med 48:830–837

Merget R, Schultze-Werninghaus G, Muthorst T, Friedrich W, Meier-Sydow J (1988) Asthma due to the complex salts of platinum–a cross-sectional survey of workers in a platinum refinery. Clin Allergy 18:569–580

Messersehmidt J, Alt F, Tolg G, Angerer J, Sehaller KH (1992) Adsorptive voltammetric procedure for the determination of platinum baseline levels in human body fluids. Fresenius J Anal Chem 343:391–394

Migliore L, Frenzilli G, Nesti C, Fontaner S, Sabbioni E (2002) Cytogenetic and oxidative damage induced in human lynmphocytes by platinum, rhodium and palladium compounds. Mutagenesis 17:411–417

Moldovan M, Palacios MA, Gómez MM, Morrison G, Rauch S, McLeod C, Ma R, Caroli S, Alimonti A, Petrucci F, Bocca B, Schramel P, Zischka M, Pettersson C, Wass U, Luna M, Saenz JC, Santamaría J (2002) Environmental risk of particulate and soluble platinum group elements released from gasoline and diesel engine catalytic converters. Sci Total Environ 296:199–208

Murdoch RD, Pepys J (1987) Platinum group metal sensitivity: reactivity to platinum group metal salts in platinum halide salt-sensitive workers. Ann Allergy 59:464–469

Murdoch RD, Pepys J, Hughes EG (1986) IgE antibody responses to platinum group metals: a large scale refinery survey. Br J Ind Med 43:37–43

Newman Taylor A (2001) Role of human leukocyte antigen phenotype and exposure in development of occupational asthma. Curr Opin Allergy Clin Immunol 1:157–161

Newman Taylor AJ, Cullinan P, Lympany PA, Harris JM, Dowdeswell RJ, du Bois RM (1999) Interaction of HLA phenotype and exposure intensity in sensitization to complex platinum salts. Am J Respir Crit Care Med 160:435–438

Niemela M, Peramaki P, Piispanen J, Poikolainen J (2004) Determination of platinum and rhodium in dust and plant samples using microwave-assisted sample digestion and ICPMS. Anal Chim Acta 521:137–142

Niezborala M, Garnier R (1996) Allergy to complex platinum salts: A historical prospective cohort study. Occup Environ Med 53:252–257

Orfao A, Ruiz-Arguelles A (1996) General concepts about cell sorting techniques. Clin Biochem 29:5–9

Óvári M, Muránszky G, Zeiner M, Virág I, Steffan I, Mihucz VG, Tatár E, Caroli S, Záray G (2007) Determination of Pt in urine of tram drivers by sector field inductively coupled plasma mass spectrometry. Microchem J 87:159–172

Palacios MA, Gómez M, Moldovan M, Gómez B (2000) Assessment of environmental contamination risk by Pt, Rh and Pd from automobile catalyst. Microchem J 67:105–113

Pepys J, Parish WE, Cromwell O, Hughes EG (1979) Specific IgE and IgG antibodies to platinum salts in sensitized workers. Monogr Allergy 14:142–145

Petrucci F, Violante N, Senofonte O, Cristaudo A, Di Gregorio M, Forte G, Alimonti A (2005) Biomonitoring of a worker population exposed to platinum dust in a catalyst production plant. Occup Environ Med 62:27–33

Petrucci F, Violante N, Senofonte O, De Gregorio M, Alimenti A, Caroli S, Forte G, Cristaudo A (2004) Development of an analytical method for monitoring worker populations exposed to platinum-group elements. Microchem J 76:131–140

Pino A, Alimonti A, Conti ME, Bocca B (2010) Iridium, platinum and rhodium baseline concentration in lichens from Tierra del Fuego (South Patagonia, Argentina). J Environ Monit 12:1857–1863

Raulf-Heimsoth M, Merget R, Rihs HP, Föhring M, Liebers V, Gellert B, Schultze-Werninghaus G, Baur X (2000) T-cell receptor repertoire expression in workers with occupational asthma due to platinum salt. Eur Respir J 16:871–878

Ravindra K, Bencs L, Van Grieken R (2004) Platinum group elements in the environment and their health risk. Sci Total Environ 318:1–43

Reale M, Vianale G, Lotti LV, Mariani-Costantini R, Perconti S, Cristaudo A, Leopold K, Antonucci A, Di Giampaolo L, Iavicoli I, Di Gioacchino M, Boscolo P (2011) Effects of palladium nanoparticles on the cytokine release from peripheral blood mononuclear cells of palladium-sensitized women. J Occup Environ Med 53:1054–1060

Rebandel P, Rudzki E (1990) Allergy to palladium. Contact Dermatitis 23:121–122

Santucci B, Valenzano C, de Rocco M, Cristaudo A (2000) Platinum in the environment: frequency of reactions to platinum-group elements in patients with dermatitis and urticaria. Contact Dermatitis 43:333–338

Schaller KH, Angerer J, Alt F, Messersschmidt J, Wever A (1992) The determination of platinum in blood and urine as a tool for the biological monitoring of internal exposure. In: Proceedings of SPIE-international society for optical engineering 1993, international conference on monitoring of toxic chemicals and biomarkers 1716: 498–504. http://proceedings.spiedigitallibrary.org/proceeding.aspx?articleid=993867. Assessed on 25 November 2013

Schierl R (2000) Environmental monitoring of platinum in air and urine. Microchem J 67:245–248

Schierl R, Fries HG, van de Weyer C, Fruhmann G (1998) Urinary excretion of platinum from platinum industry workers. Occup Environ Med 55:138–140

Schuhmacher M, Bellés M, Rico A, Domingo JL, Corbella J (1996) Impact of reduction of lead in gasoline on the blood and hair lead levels in the population of Tarragona Province, Spain, 1990–1995. Sci Total Environ 184:203–209

Schwenk M, Klein R, Templeton DM (2008) Lymphocyte subpopulations in human exposure to metals. Pure Appl Chem 80:1349–1364

SCOEL/SUM/150D (2011) Recommendation from the scientific committee on occupational exposure limits for platinum and platinum compounds. http://ec.europa.eu/social/BlobServlet?docId=7303&langId=en. Accessed on 28 November 2013

Violante N, Petrucci F, Senofonte O, Cristaudo A, Di Gregorio M, Forte G, Alimonti A (2005) Assessment of workers' exposure to palladium in a catalyst production plant. J Environ Monit 7:463–468

Wang Y, Li X (2012) International symposium on safety science and technology health risk of platinum group elements from automobile catalysts. Procedia Eng 45:1004–1009

Wiseman CL, Zereini F (2009) Airborne particulate matter, platinum group elements and human health: a review of recent evidence. Sci Total Environ 407:2493–2500

Zaray G, Ovari M, Salma I, Steffan I, Zeiner M, Caroli S (2004) Determination of platinum in urine and airborne particulate matter from Budapest and Vienna. Microchem J 76:31–34

Zereini F, Alsenz H, Wiseman CL, Püttmann W, Reimer E, Schleyer R, Bieber E, Wallasch M (2012) Platinum group elements (Pt, Pd, Rh) in airborne particulate matter in rural vs. urban areas of Germany: concentrations and spatial patterns of distribution. Sci Total Environ 416:261–268

Zereini F, Alt F, Messerschmidt J, Wiseman C, Feldmann I, von Bohlen A, Müller J, Liebl K, Püttmann W (2005) Concentration and distribution of heavy metals in urban airborne particulate matter in Frankfurt am Main, Germany. Environ Sci Technol 39:2983–2989

Zereini F, Wiseman C, Alt F, Messerschmidt J, Müller J, Urban H (2001) Platinum and rhodium concentrations in airborne particulate matter in Germany from 1988 to 1998. Environ Sci Technol 35:1996–2000

Zereini F, Wiseman C, Püttmann W (2007) Changes in palladium, platinum, and rhodium concentrations, and their spatial distribution in soils along a major highway in Germany from 1994 to 2004. Environ Sci Technol 41:451–456

Platinum Metals in Airborne Particulate Matter and Their Bioaccessibility

Clare L.S. Wiseman

Abstract Environmental concentrations of the platinum group elements (PGE) platinum (Pt), palladium (Pd) and rhodium (Rh) have been steadily increasing, due largely to their use as catalysts in automotive catalytic converters to reduce pollutant emissions. Due mainly to earlier studies which reported that PGE are most likely to be emitted in a benign metallic form, the general assumption has been that the potential health impacts of environmental exposures to these elements are limited. Recent studies on the bioaccessibility of these elements post-emission, however, both in the environment and upon uptake by organisms, indicate that concerns associated with low dose, environmental exposures are indeed warranted. The purpose of this paper is to discuss the most recent evidence pertaining to the bioaccessibility and toxic potential of environmental exposures of PGE, particularly that in airborne particulate matter (PM), the most relevant source of exposures in humans. This review is, in part, an adaptation of an article that was published in Science of the Total Environment (Wiseman and Zereini 2009).

1 Introduction

Demand for platinum group elements (PGE), most notably platinum (Pt), palladium (Pd) and rhodium (Rh), has steadily increased over the last three decades, due to their use in an ever larger number of medical and industrial applications (Matthey 2013). More recently, the addition of nanoparticulate forms of Pt to various consumer products such as foods and cosmetics, particularly in Asia, has become popular (Fröhlich and Roblegg 2012). Undoubtedly, the largest global consumer of PGE in recent decades has been the automotive catalytic converter industry, which employs Pt, Pd and Rh as catalysts to convert harmful vehicular emissions into more benign forms. Their use as exhaust catalysts has improved air quality in many

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world regions. At the same time, the application of these noble elements has led to elevated environmental concentrations of Pt, Pd and Rh, a trend which has been documented in many studies (e.g. Zereini et al. 1997, 2001, 2004; Rauch et al. 2001, 2005; Gomez et al. 2002; Bozlaker et al. 2014). Although PGE tend to be deposited in close proximity to the source of emission, accumulating in roadside environments, they also appear to be capable of long-distance transport (Barbante et al. 2001; Zereini et al. 2012a; Sen et al. 2013).

Platinum group elements are emitted in automotive exhaust together with larger alumina particles from the washcoat of the catalytic converter, due to various thermal, mechanical and chemical stressors (Schlögl et al. 1987; Artelt et al. 1999, 2000). Although they tend to be emitted in small amounts (i.e. ng/kg range), PGE have accumulated in the environment over time, with elevated concentrations being reported for airborne PM (Zereini et al. 2001, 2004, 2012a; Rauch et al. 2001, 2005, 2006; Gomez et al. 2002; Kanitsar et al. 2003; Bozlaker et al. 2014), soils (Zereini et al. 1997, 2007; Whiteley and Murray 2003) and street dust (Jarvis et al. 2001; Gomez et al. 2002; Whiteley and Murray 2003).

Of particular importance for human health, are exposures to ambient particulate matter (PM) fractions, most notably $PM_{2.5}$, which have been associated with an increased risk of morbidity and mortality in exposed urban populations (Dockery et al. 1993; Burnett et al. 1999). Metals associated with airborne PM are suspected to play a role in the many cardiorespiratory effects that have been attributed to exposures among urban populations. Documented effects include enhanced airway hyperresponsiveness, altered immune responses, ischemic heart disease, ischemic stroke and vascular and metabolic diseases (Costa and Dreher 1997; Brook et al. 2010). Most attention has been paid to metals that typically occur in higher amounts in ambient PM such as Fe, Zn and Ni. The documented occurrence of elevated levels of PGE in airborne PM fractions of concern also raises questions regarding the possible contribution of these elements to the various health outcomes linked to ambient exposures. The purpose of this paper is to assess more recent data on PGE concentrations in airborne PM, as well as their bioaccessibility and related toxic potential.

2 Platinum Metals in Airborne PM

A number of studies have demonstrated the widespread occurrence of PGE in field-collected airborne PM_{10} and $PM_{2.5}$ (see Table 1). Airborne PM collected in Gothenburg, Sweden in 1999, was reported to have mean concentrations of 14.1 pg Pt/m^3, 4.9 pg Pd/m^3 and 2.9 pg Rh/m^3 in PM_{10} and 5.4 pg Pt/m^3, 1.5 pg Pd/m^3 and 1.6 pg Rh/m^3 in $PM_{2.5}$ at a high traffic site (70,000 vehicles/day) (Rauch et al. 2001). Gomez et al. (2002) sampled PM_{10} in Madrid, Spain, Gothenburg, Sweden and Rome, Italy in 1999/2000 and reported concentrations that ranged from 7.3 to 17.7 pg Pt/m^3, 1.6–54.9 pg Pd/m^3 and 0.8–4.6 pg Rh/m^3 for all sites.

For a heavy traffic, downtown location in Vienna, Austria, Kanitsar et al. (2003) measured mean concentrations of 4.3 pg Pt/m^3, 2.6 pg Pd/m^3 and 0.4 pg Rh/m^3 for

Table 1 PGE Concentrations in Airborne PM_{10}, $PM_{2.5}$ and PM_1 (where measured)

Reference	City/country (sample year)	Sample Type	Location/description	Average PGE concentrations in pg m^{-3} (in brackets: ranges (-) or SD (±))		
				PM_{10}	$PM_{2.5}$	PM_1
Rauch et al. 2001	Gothenburg, Sweden (1999)	PM_{10} & $PM_{2.5}$	Two sites: 1. High volume (70,000 cars per day) 2. Low volume (< 10,000 cars per day)	High volume site: Pt: 14 (7.6–19) Pd: 4.9 (1.3–9.7) Rh: 2.9 (1.3–4.3) Low volume site: Pt: 2.1 (0.9–3.0) Pd: 1.8 (< 0.6–4.4) Rh: 0.6 (0.3–1.2)	High volume site: Pt: 5.4 (3.9–7.2) Pd: 1.5 (0.7–2.2) Rh: 1.6 (1.0–2.7) Low volume site: Pt: 2.7 (1.4–6.3) Pd: 1.4 (0.7–2.5) Rh: 0.5 (0.3–0.6)	N/A
Gomez et al. (2002)	Madrid, Spain (1999/2000)	PM_{10}	Downtown and ring-road locations	Downtown: Pt: 7.3 Rh: 2.8 Ring-road sites: Pt: 18 Rh: 4.6	N/A	N/A
Gomez et al. (2002)	Gothenburg, Sweden (1999/2000)	PM_{10}	Downtown and ring-road locations	Downtown Pt: 13 Pd: 4.6 Rh: 2.7 Ring-road sites: Pt: 4.1 Pd: 1.6 Rh: 0.8	N/A	N/A

(continued)

Table 1 (continued)

Reference	City/country (sample year)	Sample Type	Location/description	Average PGE concentrations in pg m^{-3} (in brackets: ranges (-) or SD (±))		
				PM_{10}	$PM_{2.5}$	PM_1
Gomez et al. (2002)	Rome, Italy (1999/2000)	PM_{10}	Downtown and ring-road locations	Downtown: Pt: 8.6 Pd: 43 Rh: 2.2 Ring-road sites: Pt: 8.1 Pd: 55 Rh: 3.0	N/A	N/A
Kanitsar et al. (2003)	Vienna, Austria (2002)	PM_{10}	Downtown, heavy traffic area	Pt: 4.3 (± 1.7) Pd: 2.6 (± 0.6) Rh: 0.4 (± 0.1)	N/A	N/A
Zereini et al. (2004)	Frankfurt, Germany (2001/2002)	PM_{10}	Three sites:1. Major street (high traffic, 32,550 cars/day), 2. Side street (low traffic, < 1 000 cars/day),3. Urban park	Major street: Pt: 16 (8.7–28) Pd: 25 (9.4–29) Rh: 2.9 (1.8–4.5) Side street: Pt: 6.2 (4.1–9.5) Pd: 8.9 (5.1–16) Rh: 0.7 (0.7–1.1) Urban park: Pt: 5.2 (3.0–7.9) Pd: 7.8 (4.7–12) Rh: 0.8 (0.3–1.5)	N/A	N/A

(continued)

Table 1 (continued)

Reference	City/country (sample year)	Sample Type	Location/description	Average PGE concentrations in pg m^{-3} (in brackets: ranges (-) or SD (±))		
				PM_{10}	$PM_{2.5}$	PM_1
Rauch et al. (2005)	Boston, USA (2002/2003)	PM_{10}	Two sites:1. > 60,000 vehicles/day2. Ca. 30,000 vehicles/day	Site 1: Pt: 9.4 (0.6–17) Pd: 11.0 (1.0–26) Rh: 2.2 (0.5–5.9) Site 2: Pt: 6.2 (0.6–36) Pd: 7.1 (0.8–39) Rh: 1.3 (0.3–5.9)	N/A	N/A
Bocca et al. (2006)	Buenos Aires, Argentina (2001)	PM_{10}	Seven inner city sites	Pt: 12.9 (2.3–48) Rh: 3.9 (0.3–17)	N/A	N/A
Rauch et al. (2006)	Mexico City, Mexico (2003)	PM_{10}	Five sites with various traffic volumes	Pt: 9.3 (± 1.9) Pd: 11 (± 4) Rh: 3.2 (± 2.2)	N/A	N/A
Zereini et al. (2012a)	Germany (2008–2010)	PM_{10}, $PM_{2.5}$ & PM_1	Three different sites: 1. Frankfurt am Main (ca. 30,000 vehicles/day, speed limit: 50 km/hr) 2. Deuselbach 3. Neuglobsow	Frankfurt am Main: Pt: 12 (1.2–81) Pd: 44 (1.2–683) Rh: 3.2 (1.1–21) Deuselbach: Pt: 2.0 (0.1–38) Pd: 2.1 (0.1–13) Rh: 1.2 (0.1–32) Neuglobsow: Pt: 1.9 (0.1–19) Pd: 2.6 (0.2–11) Rh: 0.3 (0.1–3.6)	Frankfurt am Main: Pt: 9.4 (2.6–24) Pd: 16 (5.4–27) Rh: 1.8 (0.7–4.2)	Frankfurt am Main: Pt: 3.2 (0.9–11) Pd: 8.4 (2.6–31) Rh: 0.6 (0.2–1.9)

(continued)

Table 1 (continued)

Reference	City/country (sample year)	Sample Type	Location/description	Average PGE concentrations in pg m^{-3} (in brackets: ranges (-) or SD (±))		
				PM_{10}	$PM_{2.5}$	PM_1
Bozlaker et al. (2014)	Houston, Texas (2012/2013)	PM_{10} & $PM_{2.5}$	Tunnel (ca. 20,000 vehicles/day, speed limit: 55–75 km/h)	2012: Pt: 84 (±4.7) Pd: 299 (±19) Rh: 52 (±2.7) 2013: Pt: 38 (±2.1) Pd: 130 (±8.5) Rh: 21 (±1.1)	2012: Pt: 38 (±2.1) Pd: 111 (±7.2) Rh: 17 (±0.86) 2013: Pt: 22 (±1.2) Pd: 71 (±4.6) Rh: 8.5 (±0.44)	N/A

PM_{10} sampled in 2002. In Frankfurt am Main, Germany, Zereini et al. (2004) measured average concentrations of 16 pg Pt/m^3, 25 pg Pd/m^3 and 2.9 pg Rh/m^3 in PM_{10} collected at a traffic site with ca. 30,000 vehicles/day. Platinum group element concentrations were elevated compared to a low traffic site (<1,000 vehicles/day) in the same study, with an average of 6.2 pg Pt/m^3, 8.9 pg Pd/m^3 and 0.7 pg Rh/m^3. In Frankfurt am Main, Germany, Zereini et al. (2004) sampled airborne PM at three different sites with variable traffic levels: (1) a high traffic volume site (32,500 vehicles/day), (2) a low traffic volume, side street (500–1,000 vehicles/day), and (3) park area with no traffic. For the high volume traffic site, PM_{10} samples had PGE concentrations of 16 pg Pt/m^3, 25 pg Pd/m^3 and 2.9 pg Rh/m^3. Concentrations of 6.2 pg Pt/m^3, 8.9 pg Pd/m^3 and 0.7 pg Rh/m^3 were reported for PM_{10} collected at the low traffic location. The park area had similar concentrations to the low traffic volume site, with 5.2 pg Pt/m^3, 7.8 pg Pd/m^3 and 0.8 pg/Rh m^3, an early indication of the potential for PGE to be transported with airborne PM to areas lacking in emission sources.

In Boston, Massachusetts, Rauch et al. (2005) measured PGE concentrations in PM_{10} samples collected at two different locations. Samples from the site with higher amounts of traffic (>60,000 vehicles/day) were determined to have an average concentration of 9.4 pg Pt/m^3, 11.0 pg Pd/m^3 and 2.2 pg Rh/m^3. Samples from the site with comparatively less traffic (ca. 30,000 vehicles/day) had mean values of 6.2 pg Pt/m^3, 7.1 pg Pd/m^3 and 1.3 pg Rh/m^3. In Mexico City, Rauch et al. (2006) measured concentrations of 9.3 pg Pt/m^3, 11 pg Pd/m^3 and 3.2 pg Rh/m^3 for PM_{10} collected in 2003 at five sites with variable traffic volumes. The levels of all PGE were observed to be much higher relative to that determined for PM_{10} samples collected in Mexico City 10 years earlier, 2 years following the widespread introduction of automotive catalytic converters. Bocca et al. (2006) determined mean Pt and Rh concentrations in PM_{10} in Buenos Aires of 13 pg Pt/m^3 and 3.9 pg Rh/m^3, levels comparable to those measured in other urban centres.

In a more recent study of airborne PM collected between 2008 and 2010, Zereini et al. (2012a) measured Pt, Pd and Rh levels in PM_{10}, $PM_{2.5}$ and PM_1 collected at three different locations in Germany: Frankfurt am Main, Deuselbach and Neuglobsow. In PM_{10}, the average PGE concentrations were determined to be 12 pg Pt/m^3, 44 pg Pd/m^3 and 3.2 pg Rh/m^3 at the high traffic (ca. 30,000 vehicles/day) location in Frankfurt am Main. The low traffic, rural location, Neuglobsow, had expectedly lower airborne concentrations of PGE, with 1.9 pg Pt/m^3, 2.6 pg Pd/m^3 and 0.3 pg Rh/m^3 in PM_{10}. Elemental concentrations were reported to decline with particulate size, with the lowest PGE levels measured for PM_1. Mean concentrations of PGE determined for PM_1 collected in Frankfurt am Main, for instance, were 3.2 pg Pt/m^3, 8.4 pg Pd/m^3 and 0.6 pg Rh/m^3. Compared to a previous study conducted in Frankfurt am Main (Zereini et al. 2004), PGE concentrations in airborne PM were found to be 12, 6 and 3 times greater for Pd, Pt and Rh, respectively, for samples collected in 2008–2010 compared to 2002. Most recently, elevated concentrations of PGE were reported for PM_{10} and $PM_{2.5}$ samples collected from a tunnel in Houston, Texas between 2012 and 2013 (Bozlaker et al. 2014). Of the PGE, Pd was reported to occur in the highest amounts compared to Pt and Rh in both PM_{10} and $PM_{2.5}$. Samples collected during the first sampling period had concentrations of 299 pg Pd/m^3, 84 pg Pt/m^3 and 52 pg Rh/m^3 in PM$_{10}$ and 111 pg Pd/m^3, 38 pg Pt/m^3 and 17 pg Rh/m^3 in PM$_{2.5}$. The higher PGE concentrations for airborne PM reported by Bozlaker et al. (2014) compared to other studies can be attributed to the fact that samples were collected from a tunnel, with conditions that can serve to limit the diffusion and dispersal of contaminants.

In sum, studies have consistently demonstrated the widespread occurrence of elevated PGE levels in airborne PM of biological concern, notably PM$_{10}$ and PM$_{2.5}$, in urban areas across the globe. Collectively, studies of airborne PM indicate three general trends: (1) PGE concentrations in airborne PM have risen over time since the introduction of catalytic converters, (2) Pd levels have increased relative to Pt in the last 10–20 years, as catalyst use has shifted in favour of Pd, and (3) Pd concentrations in PM$_{10}$ and PM$_{2.5}$ are often higher than for Pt in these size fractions, which suggests that human respiratory exposures are likely to be highest for Pd. While total elemental concentrations in airborne PM are important for assessing the magnitude of atmospheric contamination and exposures in mass terms, however, data regarding the potential solubility and bioaccessibilty of PGE is critical in the assessment of risk.

3 Platinum Metals: Speciation, Behavior and Bioaccessibility

While a fair amount of data on the concentrations of PGE in ambient PM has been generated over the last 10 years (e.g. Zereini et al. 1997, 2004, 2012a; Rauch et al. 2001, 2005, 2006; Gomez et al. 2002; Kanitsar et al. 2003; Bozlaker et al. 2014), current knowledge of PGE behaviour, speciation and bioavailablity following emission and uptake by organisms is limited. It has typically been assumed that PGE are emitted in a metallic form and are, thus, not bioavailable to any significant extent. In earlier dynamometer experiments, Artelt et al. (1999) reported that less than 1 % of the total Pt associated with airborne PM was soluble. In addition to measuring concentrations in exhaust condensate, this was determined by immersing tailpipe PM samples collected on glass fiber filters in an ultrasonic bath with a solution of 0.1 N HCl for 10 min. Given their study results, Artelt et al. (1999) suggested that PGEs are likely to be emitted in low toxic, insoluble (elemental) forms. Moldovan et al. (2002) conducted a series of standing bench-test experiments with various automobile models and engine types (gasoline vs. diesel powered) equipped with different types of catalytic converters. Of particular interest was the examination of catalyst ageing on PGE emissions and their solubility (with new converters vs. those that have been in use for 30,000–80,000 km). Using 0.2 mol/l HNO$_3$ as their absorbent medium, the solubility of PGE was observed to be highly heterogeneous, depending on engine type and age of catalytic converter. Generally, they determined that Pt was the least soluble, ranging between 1.4 and 19 % for gasoline powered engine models. Palladium and Rh solubility (gasoline engines) ranged between 9 and 16 % and 3 and 12 % for new catalysts, respectively. When emitted from aged catalytic converters, both elements had a solubility of virtually 100 % for gasoline-powered autos. For diesel-powered engines, Pt solubility ranged from 2 to 7 % for both new and aged catalysts, while Pd and Rh solubility varied from 10 to 37 % and 12 to 29 % for the different catalytic converters examined. In sum, experimental studies involving tailpipe sampling have demonstrated a high variability in the solubility PGE, with the bulk of direct emissions typically occurring as insoluble elemental forms.

A few studies have examined PGE solubility post-emission and the role of environmentally occurring complexing agents in modulating the behavior or bioaccessibility of these elements. Jarvis et al. (2001) conducted solubility experiments on field-collected road dust and reported a significantly higher solubility for Pd (ca. 35 %) compared to Pt and Rh in simulate rainwater (pH 3). Given the rapid dissolution observed for Pd, Jarvis et al. (2001) hypothesized that this element is not likely to be present in a metallic form following emission. They suggested that the presence of environmentally occurring complexing agents such as humic substances or chlorides could serve to transform Pd into more soluble forms. These initial studies provided a clear indication that solubility was highly variable between the respective catalysts and is influenced by a variety of different factors (e.g. age of catalyst, tailpipe- vs. field-collected samples, extract solution used). The importance of commonly occurring complexing agents in the transformation and mobilization of PGE into more bioaccessible forms was also demonstrated in a recent study by Bruder (2011), also discussed in Part III of this book. This study showed that a significant proportion of the Pt, Pd and Rh present in field-collected PM_{10} is soluble in the presence of L-Methionine and ethylenediaminetetraacetic acid (EDTA). For instance, the average solubility of Pt, Pd and Rh in airborne PM_{10} extracted with EDTA was reported to be 33, 45 and 35 % for these three elements, respectively. The measured soluble fractions in PM_{10} were much higher compared to that determined for Pt, Pd and Rh in the SRM 2557 (Used Auto Catalyst Monolith), with a solubility of <4 % for each respective element. This lends further support to previous studies which have also shown that commonly present environmental complexing agents such as humic substances can serve to increase the solubility of PGE in both lipids (Zimmermann et al. 2003) and water (Wood 1996; Lustig et al. 1998; Zimmerman et al. 2003). The Bruder (2011) study is significant for it provides indirect evidence for the presence of more soluble PGE species in ambient samples relative to that in catalyst material, which highlights the importance of using field-collected samples to assess bioaccessibility and toxicity.

To date, there have been few studies which have employed physiologically-based extraction tests to more accurately assess PGE solubility and bioaccessibility in the human body. There are two known studies which have examined PGE solubility in simulated gastrointestinal fluids (Colombo et al. 2008a; Turner and Price 2008). Only two studies have investigated PGE solubility using simulated lung fluids (i.e. artificial lysosomal fluid (ALF) and Gamble's solution) (Colombo et al. 2008b; Zereini et al. 2012b). Using two certified reference materials, Road

Dust (BCR 723, Institute for Reference Materials and Measurements (IRMM)) and Used Auto Catalyst (SRM 2557, National Institute of Standards and Technology (NIST)), Colombo et al. (2008b) demonstrated that PGE solubility was dependent on substrate, extract solution used and time of extraction. For instance, Pt solubility was ca. 36 % for the road dust compared to <8 % for the milled catalyst samples. The % solubility was lower with Gamble's solution (e.g. <0.5 % for PGEs in auto catalyst). Rhodium in road dust was the most soluble (e.g. 88 % in ALF) followed by Pd and Pt. The higher solubility for PGE in road dust compared to milled auto catalyst was attributed to the transformation of metallic species in catalytic converters to more soluble species, perhaps due to their complexation with substances commonly present in the environment such as humic compounds.

Zereini et al. (2012b) used the same simulated lung fluids, ALF and Gamble's solution, to assess the solubility of PGE in Used Auto Catalyst (SRM 2557) and field-collected airborne PM_{10}, $PM_{2.5}$ and PM_1. Similar to Colombo et al. (2008b), they observed that PGE solubility was dependent on the substrate and the extract solution used, with the highest solubility observed for PGE associated with airborne PM extracted with acidic ALF. For instance, Pt, Pd and Rh in PM_{10} extracted with ALF had mean solubilities of 23, 11 and 33 % (after 24 h). The solubility of Pt, Pd and Rh associated with PM_1 was 22, 29 and 51 %, respectively. Similarly, Zereini et al. (2012b) reported a lower solubility for PGE in SRM 2557, with <2.5 % for all PGE in both extract solutions used. Palladium was found to be the least mobile of the PGE extracted with ALF and Gamble's solution, which contrasts with previous studies using various extract solutions such as simulate rainwater (Jarvis et al. 2001).

Rhodium was shown to have the highest solubility in simulated lung fluids in the Zereini et al. (2012b) and Colombo et al. (2008b) studies. This element is generally found at the lowest environmental concentrations compared to Pt and Pd, as has been documented in many studies (e.g. Zereini et al. 2004, 2012a; Rauch et al. 2005; Bozlaker et al. 2014). Given this, a low toxic potential would normally be assumed for environmental exposures to this element. The higher relative solubility of this element is, nonetheless, of concern. The potential for Rh to become soluble and accumulate in the human body at higher concentrations should be examined further.

4 Platinum Metals and Their Toxicity

Data regarding PGE toxicity is limited, especially that which may be of relevance in terms of environmental exposures (i.e. low dose, chronic). Most of what we know regarding PGE toxicity in humans is derived from the application of Pt-containing substances as chemotherapeutic agents (IARC 1981). For example, cis-Pt, one of the most commonly used anticancer drugs in the treatment of testicular cancer, has been found to be highly nephrotoxic (Marzano et al. 2004).

The sensitizing potential of PGE via the respiratory route is generally accepted as being the most relevant for environmental exposures. Platinum salts are established allergens (Merget and Rosner 2001) and have been associated with a higher incidence of asthma, dermatitis and rhinoconjunctivitis among those occupationally exposed (Santucci et al. 2000; Cristaudo et al. 2005; Watsky 2007). The evidence for the sensitizing potential of Pd salts is limited and is believed to be low for Rh (Orion et al. 2003; Merget et al. 2010; An Goossens et al. 2011). Although it is somewhat problematic to extrapolate from high exposure, occupational conditions to low exposure, environmental levels, the sensitizing potential of ambient exposures to PGE is a human health concern. New evidence regarding the presence of a significantly higher fraction of soluble PGE species in airborne PM (Bruder 2011), possibly consisting largely in sensitizing, halogenated forms, supports this. In particular, the potential impacts of environmental exposures among those who are likely to be susceptible by virtue of their developmental stage and/or immune status (e.g. the elderly, children) or their proximity to source emissions (e.g. living next to a highway with large volumes of traffic) requires further examination.

While the greatest attention has been paid to the sensitizing potential of PGE, other toxicological endpoints may be equally relevant (Iavicoli et al. 2014). For instance, soluble Pt, Pd and Rh salts have also been demonstrated to elicit immune responses (e.g. reduced leukocyte production) in rats and chick embryos (Gagnon et al. 2006; Newkirk et al. 2014). Given their high redox potential, metal ions such as Pt(IV) can be expected to have the capacity to oxidize the sulphur contained in the amino-acid side chains of proteins. In addition, they may also form coordination complexes with proteins and cause a cascading effect involving the activation of autoreactive T cells. Platinum group elements have been demonstrated to induce the synthesis of metallothionein, a low molecular weight protein which appears to be involved in metal detoxification (Park et al. 2001). This provides indirect evidence for ability of PGE to induce an immune response upon uptake. Rhodium was recently demonstrated by Iavicoli et al. (2014) to be nephrotoxic in female Wistar rats exposed to a wide-range of occupationally- and environmentally-relevant doses in the form of Rh(III) chloride hydrate via drinking water. Although Rh occurs at the lowest environmental concentrations relative to Pt and Pd, the presence of larger soluble Rh fractions in airborne PM extracted with simulated biological fluids (Colombo et al. 2008b; Zereini et al. 2012b), highlights the need to more closely examine the potential human health effects of continuously increasing ambient levels of this element.

Compared to Pd salts, Pt has been reported to have a higher genotoxic potential in bacterial and mammalian cells (Gebel et al. 1997). A lower genotoxicity for Pd salts ($(NH_4)_2PdCl_4$, $PdCl_2$) compared to soluble Pt ($(NH_4)_2PtCl_4$, $PtCl_2$, $PtCl_4$) and Rh ($RhCl_3$) compounds has also been observed for human lymphocytes (Migliore et al. 2002). Using human bronchial epithelial cells (BEAS-2B), Schmid et al. (2007) demonstrated that inorganic PGE salts ($Pt(NO_3)_2$, $PtCl_4$, $PdSO_4$, $RhCl_3$) were capable of inducing the generation of reactive oxygen species at levels comparable to known toxic elements, Cd(II) and Cr(IV), which can impair cellular viability.

The potential in utero toxicity of PGE is not clear given the current weight of evidence but can be expected to be highly species dependent, with soluble forms being most likely to pass internal biological barriers such as the placenta. An earlier study demonstrated a limited transplacental transfer of ^{191}Pt when administered intravenously to pregnant rats, with only small amounts of ^{191}Pt occurring in fetuses (Moore et al. 1975). Gagnon and Patel (2007) showed that water-soluble, hexachloroplatinic acid (H2[PtCl6]) bioaccummulates at elevated levels in the brain and liver of chick embryos. The higher rate of accumulation for Pt in the brain tissues was attributed to the existence of an underdeveloped blood-brain barrier during early developmental stages. They also reported the induction of metallothionine (MT) synthesis in the liver and brain tissues of embryos exposed in utero to a mix of PGE (with equal amounts of Pt (H2[PtCl6]·6H2O), Pd ($PdCl_2$) and Rh($RhCl_3$) at concentrations of 0.1 and 1.0 ppm). The effects of in utero exposures to PGE in humans is difficult to predict. Many other transition metals such as Mn, Cd and Pb have been shown to be quite capable of bypassing the fetal blood-brain barrier and entering the brain through various mechanisms such as existing transport pathways or by increasing its permeability (Ek et al. 2012). Whilst the concept of an underdeveloped blood-brain barrier during fetal development has been highly contested in recent years, the susceptibility of this developmental stage to elemental exposures is widely acknowledged (Makri et al. 2004). As such, more attention should be paid to the possible impacts of chronic PGE exposures in utero.

5 Platinum Metal Exposures and Human Health

Several biomonitoring studies have been conducted to determine the body burdens of PGE in exposed subjects. In a study of bus and tram drivers (n = 178) in Munich, Germany, Schierl (2000) reported median urinary Pt values of 6.5 ng/g creatinine. Higher levels of Pt measured in the urine of several individuals were associated with the dental gold alloys. In their examination of individuals employed with the Rome City Police Force (n = 161), Iavicoli et al. (2004) reported that there were no significant differences in the urinary Pt concentrations of occupationally exposed police officers pre- and post-shift (i.e. means of 4.43 vs. 4.63 ng/l, respectively). They also determined that there were no significant differences in the urinary Pt concentrations between traffic police officers and those who conduct the bulk of their work indoors (i.e. post-shift mean of 4.64 vs. 4.63 ng/l, respectively). In contrast, Iavicoli et al. (2007) measured the urinary Pt, Rh and Pd levels in tram drivers (n = 64) in Rome and determined significantly elevated Pt, Pd and Rh concentrations compared to control subjects (n = 58), with 1.23 versus 1.03 ng Pt/g creatinine and 19.16 versus 11.18 ng Rh/g creatinine, respectively. Palladium concentrations were not, however, found to be significantly different between tram drivers (median: 11.47 ng Pd/g creatinine) and controls (median: 8.75 ng Pd/g creatinine). Interestingly, Rh levels were elevated compared to Pd and Pt in this study, despite the fact that Rh typically occurs at the lowest concentrations relative to the other PGE in ambient PM (see Zereini et al. 2004, 2012a; Bocca et al. 2006; Rauch et al. 2005, 2006).

Caroli et al. (2001) determined comparable Pt levels of <0.6–9.5 ng Pt/l in urine collected from children, whose levels were found to significantly vary with place of residence and degree of local traffic. As part of the biomonitoring efforts of PROBE (PROgramme for Biomonitoring General Population Exposure) in Italy, mean blood levels of Pd, Pt and Rh in samples collected from adolescents between 13 and 15 years (n = 45) living in the Latium region were determined to be 21.8 ng/l, 9.87 ng/l and 20.2 ng/l, respectively (Pino et al. 2012). These biomonitoring studies provide evidence that PGE body burden levels are reflective of exposures to elevated concentrations of these noble elements, with higher exposures and uptake among urban populations and those working in close proximity with traffic.

In sum, more recent evidence regarding the bioaccessibility of Pt, Pd and Rh suggests that they are a human health concern. New studies which have examined their bioaccessibility using novel methods involving the application of simulated biological fluids suggest that the toxic potential of these elements has been underestimated to date (Colombo et al. 2008b; Zereini et al. 2012b). Of particular interest, is the fact that Rh has been shown to be more soluble (Colombo et al. 2008b; Zereini et al. 2012b) and occur at higher levels in biological fluids (Iavicoli et al. 2007) in exposed subjects, despite its comparatively low occurrence in the environment. This highlights the need for more toxicity data on Rh to adequately assess its potential health effects, especially on longer term, chronic health scales.

Clearly, PGE occur at concentrations that are relatively low compared to the more abundant elements such as Cu that are present in airborne PM (Wiseman and Zereini 2014). Platinum group elements are associated with finer particle size fractions of ambient PM which have been associated with an increased incidence of morbidity and mortality in exposed urban populations (Dockery et al. 1993; Burnett et al. 1999). As such, PGE are part of a larger suite of metals which is suspected to play an important role in documented negative health outcomes. Given the fact that PGE emissions will continue, we can expect a sustained increase in the environmental accumulation of these elements far into the future. This, combined with recent evidence regarding the bioaccessibility of PGE, highlights the need for continued research and monitoring.

References

An Goossens A, Cattaert N, Nemery B, Boey L, De Graef E (2011) Occupational allergic contact dermatitis caused by rhodium solutions. Contact Dermatitis 64:158–161

Artelt S, Kock H, König HP, Levsen K, Rosner G (1999) Engine dynamometer experiments: platinum emissions from differently aged three-way catalytic converters. Atmos Environ 33:3559–3567

Artelt S, Levsen K, König HP, Rosner G (2000) Engine test bench experiments to determine platinum emissions from three-way catalytic converters. In: Zereini F, Alt F (eds) Anthropogenic platinum group element emissions their impact on man and environment. Springer-Verlag, Berlin, pp 33–44

Barbante C, Veysseyre A, Ferrari C, Van de Velde K, Morel C, Capodoglio G, Cescon P, Scarponi G, Boutron C (2001) Greenland snow evidence of large scale atmospheric contamination for platinum, palladium and rhodium. Environ Sci Tech 35:835–839

Bocca B, Caimi S, Smichowski P, Gomez D, Caroli S (2006) Monitoring Pt and Rh in urban aerosols from Buenos Aires, Argentina. Sci Total Environ 358:255–264

Bozlaker A, Spada NJ, Fraser MP, Chellam S (2014) Elemental characterization of $PM_{2.5}$ and PM_{10} emitted from light duty vehicles in the Washburn Tunnel of Houston, Texas: release of rhodium, palladium, and platinum. Environ Sci Technol 48:54–62

Brook RD, Rajagopalan S, Pope CA, Brook JR, Bhatnagar A, Diez-Rous AV, Holguin F, Hone Y, Luepker RV, Mittleman MA, Peters A, Siscovick D, Smith SC, Whitsel L, Kaufman JD (2010) Particulate matter air pollution and cardiovascular disease: an update to the scientific statement from the American Heart Association. Circulation 121:2331–2378

Bruder B (2011) Löslichkeit von Platingruppenelementen (Pt, Pd, Rh) und Schwermetallen (As, Cd, Pb, Cr, Ni, Co und Cu) im Luftstaub (PM_{10}, $PM_{2,5}$ und PM_1) in Anwesenheit von organischen Komplexbildnern. Master's Thesis, Goethe Universität Frankfurt am Main, unpublished

Burnett RT, Smith-Doiron M, Stieb D, Cakmak S, Brook JR (1999) Effects of particulate and gaseous air pollution on cardiorespiratory hospitalizations. Arch Environ Health 54:130–139

Caroli S, Alimonti A, Petrucci F, Bocca B, Krachler M, Forastiere F, Sacerdote MT, Mallone S (2001) Assessment of exposure to platinum-group metals in urban children. Spectrochim Acta B 56:1241–1248

Colombo C, Monhemius AJ, Plant JA (2008a) The estimation of the bioavailabilities of platinum, palladium and rhodium in vehicle exhaust catalysts and road dusts using a physiologically based extraction test. Sci Total Environ 389:46–51

Colombo C, Monhemius AJ, Plant JA (2008b) Platinum, palladium and rhodium release from vehicle exhaust catalysts and road dust exposed to simulated lung fluids. Ecotox Environ Safe 71:722–730

Costa DL, Dreher KL (1997) Bioavailable transition metals in particulate matter mediate cardiopulmonary injury in healthy and compromised animal models. Environ Health Persp 105:1053–1060

Cristaudo A, Sera F, Severino V, De Rocco M, Di Lella E, Picardo M (2005) Occupational hypersensitivity to metal salts, including platinum, in the secondary industry. Allergy 60:159–164

Dockery DW, Pope CA, Xu X, Spengler JD, Ware JH, Fay ME, Ferris BG, Speizer FE (1993) Association between air pollution and mortality in six US cities. N Eng J Med 329:1753–1759

Ek CJ, Dziegielewska KM, Habgood MD, Saunders NR (2012) Barriers in the developing brain and Neurotoxicology. NeuroToxicology 33:586–604

Fröhlich E, Roblegg E (2012) Models for oral uptake of nanoparticles in consumer products. Toxicology 291:10–17

Gagnon ZE, Newkirk C, Hicks S (2006) Impact of platinum group metals on the environment: a toxicological, genotoxic and analytical chemistry study. J Environ Sci Heal A 41:397–414

Gagnon ZE, Patel A (2007) Induction of metallothionein in chick embryos as a mechanism of tolerance to platinum group metal exposure. J Environ Sci Heal A 42:381–387

Gebel T, Lantzsch H, Pleßow K, Dunkelberg H (1997) Genotoxicity of platinum and palladium compounds in human and bacterial cells. Mutat Res-Gen Tox En 389:183–190

Gomez B, Palacios MA, Gomez M, Sanchez JL, Morrison G, Rauch S, McLeod C, Ma R, Caroli S, Alimonti A, Petrucci F, Bocca B, Schramel P, Zischka M, Petterson C, Wass U (2002) Levels and risk assessment for humans and ecosystems of platinum-group elements in the airborne particles and road dust of some European cities. Sci Total Environ 299:1–19

IARC (International Agency for Research on Cancer) (1981) Some antineoplastic and immunosuppressive agents: summary of data reported and evaluation. IARC monographs on the evaluation of carcinogenic risks to humans, vol 26. http://monographs.iarc.fr/ENG/Monographs/vol1-42/mono26.pdf. Accessed 10 June 2014

Iavicoli I, Bocca B, Petrucci F, Senofonte O, Carelli G, Alimonti A, Caroli S (2004) Biomonitoring of traffic police officers exposed to airborne platinum. Occup Environ Med 61:636–639

Iavicoli I, Bocca B, Carelli G, Caroli S, Caimi S, Alimonti A, Fontana L (2007) Biomonitoring of tram drivers exposed to airborne platinum, rhodium and palladium. Int Arch Occup Environ Health 81:109–114

Iavicoli I, Leso V, Fontana L, Marinaccio A, Bergamaschi A, Calabrese EJ (2014) The effects of rhodium on the renal function of female Wistar rats. Chemosphere 104:120–125

Jarvis K, Parry S, Piper M (2001) Temporal and spatial studies of autocatalyst-derived platinum, rhodium, and palladium and selected vehicle-derived trace elements in the environment. Environ Sci Technol 35:1031–1036

Matthey Johnson (2013) Platinum- annual report. Johnson Matthey, London, p 104

Kanitsar K, Koellensperger G, Hann S, Limbeck A, Puxbaum H, Stingeder G (2003) Determination of Pt, Pd and Rh by inductively coupled plasma sector field mass spectrometry (ICP-SFMS) in size-classified urban aerosol samples. J Anal At Spectrom 18:239–246

Lustig S, Zang S, Beck W, Schramel P (1998) Dissolution of metallic platinum as water soluble species by naturally occurring complexing agents. Microchim Acta 129:189–194

Makri A, Goveia M, Balbus J, Parkin R (2004) Children's susceptibility to chemicals: a review by developmental stage. J Toxicol Environ Health B 7:417–435

Marzano C, Bettio F, Baccichetti F, Trevisan A, Giovagnini L, Fregona D (2004) Antitumor activity of a new platinum(II) complex with low nephrotoxicity and genotoxicity. Chem Biol Interact 148:37–48

Merget R, Rosner G (2001) Evaluation of the health risk of platinum group metals emitted from automotive catalytic converters. Sci Total Environ 270:165–173

Merget R, Sander I, Van Kampen V, Raulf-Heimsoth M, Ulmer H-M, Kulzer R, Bruening T (2010) Occupational immediate-type asthma and rhinitis due to rhodium salts. Am J Ind Med 53:42–46

Migliore L, Frenzilli G, Nesti C, Fortaner S, Sabbioni E (2002) Cytogenic and oxidative damage induced in human lymphocytes by platinum, rhodium and palladium compounds. Mutagenesis 17:411–417

Moldovan M, Palacios MA, Gomez MM, Morrison G, Rauch S, McLeod C, Ma R, Caroli S, Alimonti A, Petrucci F, Bocca B, Schramel P, Zischka M, Pettersson C, Wass U, Luna M, Saenz JC, Santamaría J (2002) Environmental risk of particulate and soluble platinum group elements released from gasoline and diesel engine catalytic converters. Sci Total Environ 296:199–208

Moore W, Hysell D, Crocker W, Stara J (1975) Biological fate of a single administration of ^{191}Pt in rats following different routes of exposure. Environ Res 9:152–158

Newkirk CE, Gagnon ZE, Pavel Sizemore IE (2014) Comparative study of hematological responses to platinum group metals, antimony and silver nanoparticles in animal models. J Environ Sci Health A Tox Hazard Subst Environ Eng 49:269–280

Orion E, Matz H, Wolf R (2003) Palladium allergy in an Israeli contact dermatitis clinic. Contact Dermatitis 49:216–217

Park JD, Lui Y, Klaassen CD (2001) Protective effect of metallothionein against the toxicity of cadmium and other metals. Toxicology 163:93–100

Pino A, Amato A, Alimonti A, Mattei D, Bocca B (2012) Human biomonitoring for metals in Italian urban adolescents: Data from Latium Region. Int J Hyg Environ Health 215:185–190

Rauch S, Lu M, Morrison GM (2001) Heterogeneity of platinum group metals in airborne particles. Environ Sci Technol 35:595–599

Rauch S, Hemond HF, Peucker-Ehrenbrink B, Ek KH, Morrison GM (2005) Platinum group element concentrations and osmium isotopic composition in urban airborne particles from Boston, Massachusetts. Environ Sci Technol 39:9464–9470

Rauch S, Peucker-Ehrenbrink B, Molina LT, Molina MJ, Ramos R, Hemond H (2006) Platinum group elements in airborne particles in Mexico City. Environ Sci Technol 40:7554–7560

Santucci B, Valenzano C, de Rocco M, Cristaudo A (2000) Platinum in the environment: frequency of reactions to platinum-group elements in patients with dermatitis and urticaria. Contact Dermatitis 43:333–338

Schierl R (2000) Environmental monitoring of platinum in air and urine. Microchem J 67:245–248

Schlögl R, Indlekofer G, Oelhafen P (1987) Mikropartikelemissionen von Verbrennungsmotoren mit Abgasreinigung, Röntgen-Photoelektronenspektroskopie in der Umweltanalytik. Angew Chem 99:312–322

Schmid M, Zimmermann S, Krug HF, Sures B (2007) Influence of platinum, palladium and rhodium as compared with cadmium, nickel and chromium on cell viability and oxidative stress in human bronchial epithelial cells. Environ Int 33:385–390

Sen IS, Peucker-Ehrenbrink B, Geboy N (2013) Complex anthropogenic sources of platinum group elements in aerosols on Cape Cod, USA. Environ Sci Technol 47:10188–10196

Turner A, Price S (2008) Bioaccessibility of platinum group elements in automotive catalytic converter particulates. Environ Sci Technol 42:9443–9448

Watsky KL (2007) Occupational allergic contact dermatitis to platinum, palladium and gold. Contact Dermatitis 57:382–383

Whiteley JD, Murray F (2003) Anthropogenic platinum group element (Pt, Pd and Rh) concentrations in road dusts and roadside soils from Perth, Western Australia. Sci Total Environ 317:121–135

Wiseman CLS, Zereini F (2009) Airborne particulate matter, platinum group elements and human health: a review of recent evidence. Sci Total Environ 407:2493–2500

Wiseman CLS, Zereini F (2014) Characterizing metal(loid) solubility in airborne PM_{10}, $PM_{2.5}$ and PM_1 in Frankfurt, Germany using simulated lung fluids. Atmos Environ 89:282–289

Wood SA (1996) The role of humic substances in the transport and fixation of metals of economic interest (Au, Pt, Pd, U, V). Ore Geol Rev 11:1–31

Zereini F, Skerstupp B, Alt F, Helmers E, Urban H (1997) Geochemical behaviour of platinum-group elements (PGE) in particulate emissions by automobile exhaust catalysts: experimental results and environmental investigations. Sci Total Environ 206:137–146

Zereini F, Wiseman C, Alt F, Messerschmidt J, Müller J, Urban H (2001) Platinum and rhodium concentrations in airborne particulate matter in Germany from 1988 to 1998. Environ Sci Technol 35:1996–2000

Zereini F, Alt F, Messerschmidt J, von Bohlen A, Liebl K, Püttmann W (2004) Concentration and distribution of platinum group elements (Pt, Pd, Rh) in airborne particulate matter in Frankfurt am Main, Germany. Environ Sci Technol 38:1686–1692

Zereini F, Wiseman C, Püttmann W (2007) Changes in palladium, platinum and rhodium concentrations and their spatial distribution in soils along a major highway in Germany from 1994 to 2004. Environ Sci Technol 41:451–456

Zereini F, Alsenz H, Wiseman CLS, Püttmann W, Reimer E, Schleyer R, Bieber E, Wallasch M (2012a) Platinum group elements (Pt, Pd, Rh) in airborne particulate matter in rural versus urban areas of Germany: concentrations and spatial patterns of distribution. Sci Total Environ 416:261–268

Zereini F, Wiseman CLS, Püttmann W (2012b) In vitro investigations of platinum, palladium, and rhodium mobility in urban airborne particulate matter (PM_{10}, $PM_{2.5}$, and PM_1) using simulated lung fluids. Environ Sci Technol 46:10326–10333

Zimmermann S, Menzel CM, Stüben D, Taraschewski H, Sures B (2003) Lipid solubility of the platinum group metals Pt, Pd and Rh in dependence on the presence of complexing agents. Environ Pollut 124:1–5

Occupational Health Aspects of Platinum

Rudolf Schierl and Uta Ochmann

Abstract Human health risks at workplaces in platinum industry can emerge from inhalative exposure, explicitly allergic asthma caused by halogenated complex platinum salts. Airborne concentrations of platinum (Pt) are varying (up to 20 µg Pt/m^3) among workplaces, but reliable ambient measurements are not easy because of short-term concentration peaks and sensitisation to platinum salts can occur even in low exposure levels. Biological monitoring of Pt in urine gives clear evidence for exposure because values are 100–1,000-fold higher compared to unexposed population (1–10 ng/l). Regular medical examinations are recommended to determine specific sensitisation and work related allergic symptoms. In pharmacies and hospital care units cancerogenic platinum compounds like the drug cisplatin are handled in cancer therapy. In such settings exposure levels are low and urinary Pt concentrations close to those of unexposed people. Therefore, confounders like dental noble metal alloys can have a significant influence and have to be taken in account. Wipe samples have been introduced in pharmacies and hospitals and are an appropriate method to detect contaminated spots and help to reduce exposure to cancerogenic platinum compounds through improvement of work place safety measures.

1 Introduction

Human health risks at the workplace concerning platinum and platinum compounds can emerge mainly from dermal and inhalative exposure. Two risks are in the main focus, explicitly allergic asthma caused by halogenated complex platinum salts, and cancer risks from platinum anti-neoplastic agents like cisplatin. Therefore, we would like to concentrate in this chapter on platinum industry sector and on

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pharmacy/hospital settings. Thus, this chapter describes current aspects in those fields of research. More information about workplace and environmental biomonitoring of platinum group elements (PGEs) is summarized in the book chapter written by Ivo Iavicoli and Veruscka Leso.

2 Health Risks

2.1 Platinum Industry

Main occupational exposures to platinum salts occur in platinum refineries and during manufacturing of catalysts, mostly in automotive industry. Mined platinum ore and recycled metal are treated with aqua-regia to generate hexachloroplatinic acid, which is the basic compound of many other soluble platinum salt compounds. Halogenated complex platinum salts can induce type 1-sensitisation. Clinical allergic symptoms are conjunctivitis, rhinitis, asthma and contact urticaria. Studies in catalyst production plants demonstrate a correlation of the exposure level and the incidence of platinum salt related allergic diseases in exposed workers (Merget et al. 2000).

More than 100 years ago exposure to platinum salts at the workplace has received attention for the first time in occupational medicine because of allergic airway reactions (Karasek and Karasek 1911). In addition, skin eczema induced by type 4-sensitisation (prolonged T-cell associated immune reaction) to platinum salts is described. In the platinum industry the incidence of allergic symptoms is about 20 %, with an increased ratio in smokers (Niezborala and Garnier 1996; Venables et al. 1989). In summary, an association between exposure of workers to halogenated platinum salts and the development of allergic sensitization is indicated by numerous case reports and epidemiology studies (e.g. Calverley et al. 1995; Merget et al. 2000; Niezborala and Garnier 1996; Venables et al. 1989).

Halogenated Pt salts are generally considered soluble and both their solubility and toxicity appear to be related to the halogen-ligands coordinated to Pt and the negative charge of these complexes (Rosner and Merget 1999). There is a difference between the halogenated Pt salts and platinum dichlorotetramine ($[Pt(NH_3)_4]Cl_2$), a platinum compound in which halides are present as ions. There seems to be no allergic potential for this frequently used platinum dichlorotetramine compound (Linnett and Hughes 1999).

2.2 Health Care Settings

Occupational exposures to platinum-based antineoplastic drugs like cisplatin, carboplatin and oxaliplatin are to be considered in production, preparation and application. Furthermore, health care workers in contact to patients treated with platinum-based antineoplastic drugs can be exposed through contact to sweat, urine and other excretions.

The antineoplastic drug cisplatin (cis-dichloro-diammine-platinum(II)), which was introduced by Rosenberg et al. (1965), is administered in the case of several cancers and is most effective against testicular cancer, where 90 % of the patients—mostly young men—can be cured completely (e.g. Hohnloser et al. 1996). Since then, platinum-based antineoplastic drugs have become an important component in chemotherapy protocols for the treatment of ovarian, testicular, lung and bladder cancers, as well as lymphomas, myelomas and melanoma. The mechanism of these drugs is in principle an inter- and intra-strand complexation of Guanine in the DNA molecule (Eastman 1986). But the drugs are mutagenic and carcinogenic themselves (IARC 1987). Special handling precautions by pharmaceutical and hospital personnel are therefore mandatory.

Cisplatin has been classified by the International Agency for Research on Cancer (IARC 1987) in cancer Group 2A, i.e. probably carcinogenic to humans, based on inadequate evidence of carcinogenicity in humans and sufficient evidence of carcinogenicity in animals (increased incidence of tumours in rats (leukaemia) and mice (lung adenomas) following multiple intraperitoneal injections). Although no cancer bioassays are available for other platinum antitumor drugs, mutagenicity assays suggest possible carcinogenic activity similar to that of cisplatin (Sanderson et al. 1996).

There are no publications reporting cancer cases in cisplatin exposed pharmacy and health care personnel. This is not surprising because significant exposure to cisplatin alone is not the case commonly. In most health care settings personnel is exposed to many pharmaceuticals with cancerogenic, mutagenic and reproductive risks. Furthermore, the cocktail of administered substances has been changed permanently and staff tasks and protection as well. Nevertheless, a Dutch committee (DECOS 2005) has defined additional cancer risks for airborne cisplatin: A workplace exposure (8 h) to 50 ng/m^3 cisplatin over 40 years will cause 4×10^{-5} additional cancers related to cisplatin, which was designated as acceptable risk.

3 Evaluation of Exposure

3.1 Platinum Industry

3.1.1 Workplace Air Monitoring

In noble metal industry, there are some work-places (e.g. refining, catalyst coating, handling of platinum salts) with elevated platinum exposure.

Because inhalation is the most important path of uptake, measurement of airborne concentrations of platinum compounds is a necessary tool for controlling work place exposure. But this technique has some difficulties which have to be taken into account:

- Representative position of samplers in big factory halls (ambient monitoring)
- Mounting workers with personal monitors (position, duration)
- Choosing the appropriate filter material (field blinds, digestion)
- Determination of the concentration of total platinum or compound species or soluble fraction.

Additionally, other factors like numbers of samples, costs of analytics have to be clarified. Generally, personal samplers show higher concentrations by a factor of 3–10 compared to area samplers.

During some manufacturing procedures, airborne concentrations of platinum and platinum salts are near threshold limit values (TLVs). Maynard et al. (1997) and Schierl et al. (1998) measured mean Pt concentrations (8 h average) from 0.03 up to 2.2 μg/m^3 with peak Pt concentrations up to 26 μg/m^3.

The legal airborne permissible exposure limit for soluble platinum salts issued by OSHA (2011) is 2 μg Pt/m^3 averaged over an 8-h work shift. The UK Health and Safety Executive (HSE) and the American Conference of Governmental Industrial Hygienists (ACGIH) advised the same exposure limit. The MAK Commission of the German Research Foundation suspended the MAK-value of 2 μg Pt/m^3 because of the high sensitisation potential. Based on the endpoint of the respiratory sensitisation effects of chloroplatinates the Health Council of the Netherlands Expert Committee on Occupational Standards (DECOS) published (2008) a recommendation for an occupational exposure limit (OEL) for chloroplatinates of 0.005 μg/m^3 (measured as total platinum), as an 8-h time-weighted average concentration.

3.1.2 Biological Monitoring

In humans, absorbed platinum is excreted in the urine, whereby 20–45 % of it is eliminated within 24 h after its intake (Schierl et al. 1998). In several investigations about background concentrations, people being only environmentally exposed to platinum showed urine concentration between 1.1 and 6.3 ng/L. Dental alloys containing precious metals lead to higher urine concentrations in adults up to 100 ng/L (UBA 2003).

Different sensitive analytic methods exist to determine platinum levels in urine in this very challenging ppt concentration range. Routinely, double-focusing sector field mass spectrometry with inductively coupled plasma (SF-ICP-MS) and voltammetry have shown to be appropriate, but both methods have to be performed under strict internal and external quality schemes. Details about analytical techniques are summarized in another book chapter (Review by Roland Schindl and Kerstin Leopold).

The urinary platinum excretion of industrial workers in a German plant showed elevated levels up to 6,270 ng Pt/g creatinine (Schierl et al. 1998). The mean urinary platinum excretion of this study group resulted in 1994 ng Pt/g creatinine which is 500-fold above the median of the control and unexposed persons (Krachler et al. 1998; Messerschmidt et al. 1992; Schramel et al. 1995). Three former employees had elevated urinary excretion levels even several years after last exposure to platinum. This can be explained by a long-term storage of some amounts of incorporated platinum (Hohnloser et al. 1996).

In a big study about industrial noble metal exposure (Petrucci et al. 2005; Cristaudo et al. 2005) airborne platinum concentration ranged from 0.02 to 1.21 µg/m^3 measured by area samplers. Personal sampling resulted in higher concentrations up to 6 µg/m^3. The proportion of soluble platinum ranged from 2 to 43 %. Mean urinary platinum concentrations varied from 100 ng/l (corresponds approximately to 80 ng/g creatinine) for administration employees up to 1,900 ng/l (ca. 1,500 ng/g creatinine) for washcoat workers. Platinum concentrations in hair samples correlated well with urinary excretion but blood samples seemed to be not as relevant.

In a recent doctoral thesis (Korntheuer 2013) airborne and urinary platinum concentrations over 10 years (1999–2009) from a company of the Pt industry sector have been appraised. It was clearly shown that there are big differences in urinary platinum excretion depending on specific exposure scenarios (Fig. 1). Exposure to soluble platinum salts is an important factor, but also high exposure to platinum metal can lead to a significant uptake into the body. Looking to the time course over 10 years a trend to lower urinary platinum excretions from workers was seen and documented better protection of workers (data not shown).

The correlation of airborne to urinary platinum concentrations is not simple at all. The main reason is that airborne measurements are varying very much concerning position and peak concentrations. Personal sampling shows frequently concentrations 2–10 times higher than area samplers (Korntheuer 2013). Also short-term peak exposures, which could be important for sensitized people, are difficult to detect. An important step forward to improve the correlation of airborne to urinary platinum concentrations was to focus on soluble platinum only. Figure 2 shows a correlation between airborne soluble platinum concentrations and urinary platinum excretion. The single points represent median values at specific workplaces and result in a moderate linear correlation by a log/log diagram.

3.2 Health Care Settings

3.2.1 Workplace Air Monitoring

Generally, airborne concentrations of cytostatic platinum compounds are very low in pharmacy or hospital settings. But there is always a risk of spillages and cross-contaminations around the workplaces. Additionally, significant contamination by platinum-drugs at the outside of vials has been detected (Connor et al. 2005;

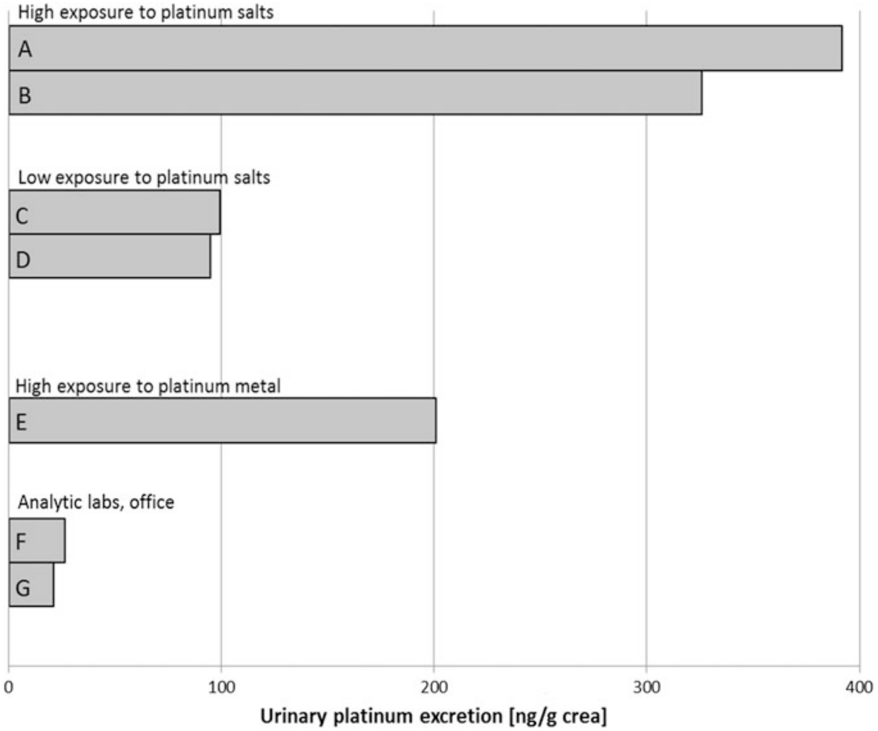

Fig. 1 Exemplary urinary platinum excretion (ng/g creatinine) from workers exposed to different airborne platinum concentrations (A-G different workplaces)

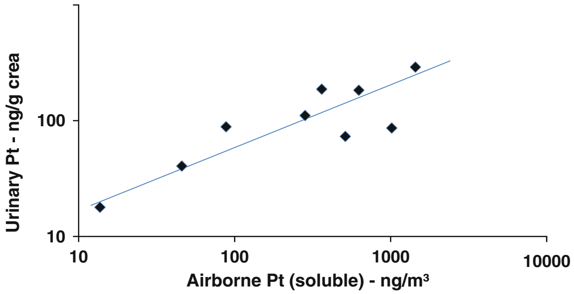

Fig. 2 Log/log diagram for the correlation of airborne soluble platinum concentrations (personal sampling) and urinary platinum excretion

Nygren et al. 2002; Mason et al. 2003). Several years ago wipe sampling has been introduced as an effective tool in order to detect contaminations by platinum-drugs (Brouwers et al. 2007; Schmaus et al. 2002). A study in two UK pharmacies confirmed that wipe samples are more effective in detecting contaminated spots than airborne sampling (Mason et al. 2005). The assumption that low contamination around pharmacies will lead to low biological uptake from cytostatic drugs by personnel was confirmed by a recent study in Italy (Sottani et al. 2010). Furthermore, guidance values have been introduced in order to allow benchmarking in pharmacy settings (Schierl et al. 2009). Those values have been defined statistically from a big dataset for platinum (as marker for cis/carbo/oxaliplatin, n = 1008). The 50 and 75th percentiles were calculated and evaluated (Table 1).

Following this concept, contamination in many pharmacies have been reduced to a great extent during the last years. Meanwhile locations from heath care settings have been monitored as well and again significant contamination of platinum on several locations (infusion equipment, waste bins, patient's toilets etc.) were detected (Kopp et al. 2013). For several years hyperthermic intraperitoneal chemotherapy (HIPEC) has been applied for treatment of specific cancers. By this technique during operation the open abdomen is perfused with warm (41°C) solutions of cisplatin or oxaliplatin over 1 h. First measurements of contamination risks have been performed (Schierl et al. 2012) but more studies are needed to cover potential risks of the whole procedure.

3.2.2 Biological Monitoring

In a detailed study about 100 employees from 14 hospital pharmacies and two oncology departments were monitored over a 3 years period (Pethran et al. 2003). From each participant urine samples over a 24-h period were collected separately; at the end of a working shift and the following Monday morning. Additionally, spot urine samples after a 3 week holiday were analysed. In total, the platinum concentration in nearly 1,500 samples has been determined. Mean and median values after holidays and after weekends are very similar, but significantly lower compared to working-shift samples. Obviously, there has been an incorporation of some platinum-drug during work for at least 20 % of the staff. Although the increased platinum concentrations (5–40 ng/l) are rather low when compared with platinum industry workers (see Sect. 2.1.2), there is still concern because of the carcinogenic potential of cisplatin. During this investigation it was detected that dental gold alloys are an important confounder associated with biological monitoring of platinum in urine (Schierl 2001). The mobilisation of such tiny amounts of platinum

Table 1 Guidance values for contamination detected by wipe sampling ([contaminant] = concentration of the contaminant in the wipe sample, Q2 = 50th percentile, Q3 = 75th percentile)

Percentiles	Platinum (pg/cm^2)	Evaluation	Traffic light
(Platinum) < Q2	0.6	Usual contamination	Green
Q2 < (platinum) < Q3	0.7–3.9	Pay attention	Yellow
Q3 < (platinum)	4.0	Contamination is high	Red

(gold and other metals as well) has no health relevance in general but is very important for the evaluation of "low level exposures". Meanwhile, silicone implants have also been identified as potential "background" source of elevated urinary platinum excretion (Schierl et al. 2014). Therefore, a single determination of urinary platinum without knowledge of the "individual background value" can lead to false interpretation of supposed occupational exposures. These difficulties have been confirmed by a study about urinary platinum excretion from pharmacy technicians in UK (Mason et al. 2005). Identification of the Pt origin by analysis of the speciation of platinum compounds in urine is no option because cisplatin is excreted as chloro-aqua-complexes (Hann et al. 2005).

Only in case of elevated airborne platinum-drug concentrations biological monitoring seems to be a good decision. In a pharmacy they prepared a cisplatin stock solution by handling of 10 g cisplatin powder. Weighing and filling operations have been done without protection. Measuring of airborne Pt resulted in 1.0–3.0 μg/m^3. Consequently, urinary platinum concentration of the involved pharmacist was elevated immediately after the procedure (Fig. 3). After discussing this result with the pharmacy staff the whole procedure was performed in a hood (Berner Box). Subsequently, urinary Pt-concentrations were found much lower compared to the unprotected procedure. Also airborne platinum concentrations were significantly lower (0.001–0.02 μg/m^3) during the improved procedure. Such investigations help local staff very much in optimization of workplace procedures.

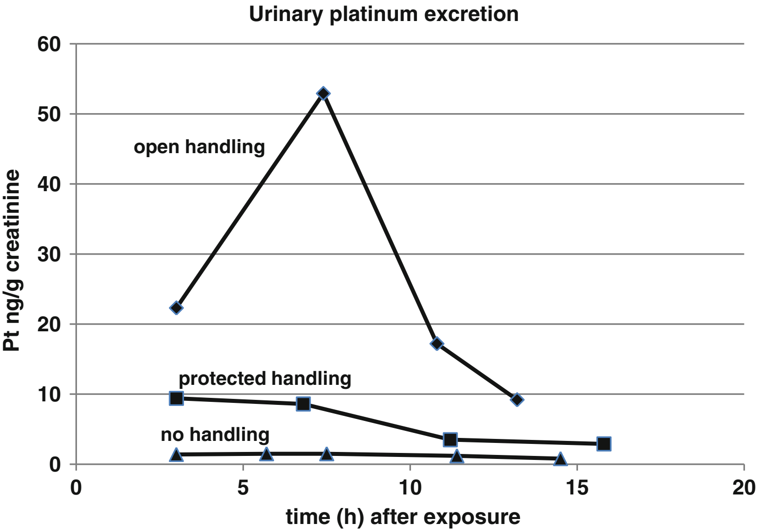

Fig. 3 Urinary platinum excretion in spot urine samples after handling cisplatin powder on a desk (open handling, *rhomb*) and in a hood (protected handling, *square*) compared to no handling (*triangle*)

4 Precaution for Employees

4.1 Platinum Industry

4.1.1 Biological Monitoring

The determination of platinum in urine is an important tool to evaluate exposure from individual worker in various work places. Unfortunately, limit values for urine concentrations of platinum do not exist. The German Federal Environmental Agency (UBA) recommended a reference value of 10 ng/L (ca. 8 ng/creatinine) for people without dental gold alloys (UBA 2003). As mentioned above, urinary and air concentration of soluble platinum salts correlate, but even in low exposure levels sensitisation can occur and therefore a prediction of individual risk by biological monitoring is not possible.

4.1.2 Individual Preventive Medical Examination

Because of underlying immunologic mechanisms of type-1 sensitisation, a regular screening program for all exposed workers should be implemented irrespective of the exposure level. This program should include biomonitoring of platinum and teaching of necessary safety measures and typical clinical allergic symptoms to create a better awareness of the exposed workers. In addition, a skin prick test can be performed with diluted hexachloroplatinic acid (detailed information can be obtained from International Platinum Group Metals Association e.V. (IPA), Schießstättstraße 30, 80339 Munich, Germany).

The application of the skin prick test should be limited to trained personnel. The primary indication for the skin prick test is the further clinical investigation of work related symptoms but it can also be used for detecting a sensitisation before emerging symptoms. The skin prick test is not eligible for testing the occupational aptitude during pre-employment medical examination. A solely positive skin prick test signals an elevated risk for developing an allergy. In this situation, advanced work safety measures should be initiated like transferring the worker to a workplace with low or none exposure and intensifying screening examinations.

Bronchial symptoms should be diagnosed according to asthma guideline. Workers with a diagnosed platinum salt related allergic disease should cease exposure completely even if symptoms are limited to urticaria, conjunctivitis or rhinitis. The risk for an additional developing of allergic asthma is high if they stay exposed. Like any other work related allergy, prognosis of platinum allergic asthma worsens in correlation to the time having worked in exposure with symptoms.

Recommendation for medical examination program

Before starting work in exposure to Platinum:

- Case history:
  Allergic symptoms (rhinitis, bronchial tightness, coughing, wheezing, dyspnea, conjunctivitis, dermal symptoms like eczema, itching):
  seasonal and/or all-season, ever work related?
  Ever allergy diagnostics carried out? If yes, collect results.
- Lung function testing
- Testing of bronchial hyperreactivity
- Teaching of necessary safety measures and typical clinical allergic symptoms

3–6 months after start of work in exposure to Platinum (shortly after several exposure shifts):

- Case history:
  Work related allergic symptoms (as mentioned above)?
- Biological monitoring Platinum in urine
- Skin prick test Platinum
- Reassessment of lung function is only necessary if bronchial symptoms are reported
- Teaching of necessary safety measures and typical allergic symptoms

Repetition of this follow-up examination in dependence of results: No allergic symptoms, normal biomonitoring and normal skin prick test: 2 years. Contemporary medical consultation whenever work related allergic symptoms emerge. Elevated biological monitoring values do not indicate a higher risk for sensitisation but can reflect insufficient working conditions. An inspection of the working area should be carried out by occupational safety professionals. Monitoring should be repeated within 3 months.

Persons exhibiting a positive Platinum skin prick test without any allergic symptoms should be offered a workplace with very low or none exposure to Platinum salts.

Persons with newly reported work related allergic symptoms should receive comprehensive diagnostics. In case of an additionally positive skin prick test, occupational disease is to be considered.

4.1.3 Workplace safety measures

In consequence, the main task of workplace safety measures is to reduce the inhalative exposure by technical means like working with closed production systems and using sufficient exhausting techniques. Dermal exposure can be avoided by wearing appropriate gloves and clothing with long sleeves. Exposure at the workplace can be monitored by measuring airborne platinum concentrations and the incorporated platinum. Latter is done by biomonitoring of urinary platinum after a shift. Both measurements show a close correlation (Petrucci et al. 2005; Schierl et al. 1998).

4.2 Health Care Settings

4.2.1 Biological Monitoring

A routine biological monitoring is not advisable because of non-defined exposure limits, low urinary platinum concentrations and relevant confounders like dental alloys. But in case of a work accident or supposed higher exposure, biological monitoring of urinary platinum can be conducted in order to quantify the exposure.

4.2.2 Individual Preventive Medical Examination

There is no evidence for a reasonable preventive medical examination. Avoidance of exposure is the most important measure. Frequent instructions and control of working habits are essential. Because of potential carcinogenicity, exposure limits cannot be issued. Employers are required to minimize exposure by technical means in first line. Women should not be exposed at all during pregnancy and breast feeding.

4.2.3 Workplace Safety Measures

Exposure during production of platinum based drugs can be reduced by setting high hygiene standards and by using sufficient facilities (e.g. biological safety cabinets, isolators) as well as personal protection equipment. Preparation and application of anti-neoplastic drugs is mostly done by pharmacy and health care workers. Finished products without the necessity of dilution and blending would help to minimize their exposure. Nevertheless, contamination of wrapping can occur during production, so wearing of gloves during handling is compulsory. Hygiene measures in clinics and pharmaceutical production can be controlled by wipe samples (see Sect. 2.2.1).

Recommendation for improvement of work safety

Pharmacy settings

Evaluation of workplaces to identify and assess risks for hazards.
Regular reviewing of current inventories of hazardous drugs, equipment, and practices.
Implementation of SOPs for safely handling of hazardous drugs at work.
Implementing of regular training reviews with all potentially exposed workers, including cleaning up of spills, and using of all equipment and PPE properly.

Application settings (hospitals, day care units)

Strictly use of gloves during all procedures (not forget changing).
Sufficient rinsing (min 100 ml) of infusion lines after application.
Patients excretions (urine, sweat etc.) are contaminated, pay attention.
Separate cleaning equipment for patient’s toilets, which are contaminated.
More detailed information and an exhaustive overview about publications and recommendations are supplied by NIOSH:
http://www.cdc.gov/niosh/topics/antineoplastic/pubs.html#b

References

Brouwers EEM, Huitema ADR, Bakker EN, Douma JW, Schimmel KJM, van Weringh G, de Wolf PJ, Schellens JHM, Beijnen JH (2007) Monitoring of platinum surface contamination in seven Dutch hospital pharmacies using inductively coupled plasma mass spectrometry. Int Arch Occup Environ Health 80:689–699

Calverley AE, Rees D, Dowdeswell RJ, Linnett PJ, Kielkowski D (1995) Platinum salt sensitivity in refinery workers: incidence and effects of smoking and exposure. Occup Environ Med 52:661–666

Connor TH, Sessink PJ, Harrison BR, Pretty JR, Peters BG, Alfaro RM, Bilos A, Beckmann G, Bing MR (2005) Surface contamination of chemotherapy drug vials and evaluation of new vial-cleaning techniques: results of three studies. Am J Health Syst Pharm 62:475–484

Cristaudo A, Sera F, Severino V, De Rocco M, Di Lella E, Picardo M (2005) Occupational hypersensitivity to metal salts, including platinum, in the secondary industry. Allergy 60:159–164

Dutch Expert Committee on Occupational Standards (DECOS) (2005) Cisplatin, health-based recommended occupational exposure limit. DECOS, a committee of the Health Council of the Netherlands, No. 2005/03OSH, The Hague

Dutch Expert Committee on Occupational Standards (DECOS) (2008) Platinum and platinum compounds, Health-based recommended occupational exposure limit. DECOS, a committee of the Health Council of the Netherlands, No. 2008/12OSH, The Hague

Eastman A (1986) Reevaluation of interaction of cisdichloro(ethylenediamine)platinum(II) with DNA. Biochemistry 25:3912–3919

Hann S, Stefanka Z, Lenz K, Stingeder G (2005) Novel separation method for highly sensitive speciation of cancerostatic platinum compounds by HPLC-ICP-MS. Anal Bioanal Chem 381:405–412

Hohnloser JH, Schierl R, Hasford B, Emmerich B (1996) Cisplatin based chemotherpay in testicular cancer patients: Long term platinum excretion and clinical effects. Eur J Med Res 1:509–514

International Agency for Research on Cancer (IARC) (1987) Overall evaluations of carcinogenity: an updating of IARC Monograph vol 1–42. IARC Monogr Suppl 7:170–171

Karasek SR, Karasek M (1911) Report of the Illinois state commission of occupational diseases to his excellency governor Charles S Deneen. Warner Printing Company, Chicago 97

Kopp B, Schierl R, Nowak D (2013) Evaluation of working practices and surface contamination with antineoplastic drugs in outpatient oncology health care settings. Int Arch Occup Environ Health 86(1):47–55

Korntheuer (2013) Platinkonzentrationen in Urin- und Luftproben zur Abschätzung der inneren Belastung von Beschäftigten in der Edelmetallindustrie. Dissertation University Munich (LMU)

Krachler M, Alimonti A, Petrucci F, Irgolic KJ, Forastiere F, Caroli S (1998) Analytical problems in the determination of platinum-group metals in urine by quadrupole and magnetic sector field inductively coupled plasma mass spectrometry. Anal Chim Acta 363(1):1–10

Linnett PJ, Hughes EG (1999) 20 years of medical surveillance on exposure to allergenic and non-allergenic platinum compounds: the importance of chemical speciation. Occup Environ Med 56(3):191–196

Mason HJ, Blair S, Sams C, Jones K, Garfitt SJ (2005) Exposure to antineoplastic drugs in two UK hospital pharmacy units. Ann Occup Hyg 49:603–610

Mason HJ, Morton J, Garfitt SJ, Iqbal S, Jones K (2003) Cytotoxic drug contamination on the outside of vials delivered to a hospital pharmacy. Ann Occup Hyg 47:681–685

Maynard AD, Northage C, Hemingway M, Bradley SD (1997) Measurement of short-term exposure to airborne soluble platinum in the platinum industry. Ann Occup Hyg 41:77–94

Merget R, Kulzer R, Dierkes-Globisch A, Breitstadt R, Gebler A, Kniffka A, Artelt S, Koenig HP, Alt F, Vormberg R, Baur X, Schultze-Werninghaus G (2000) Exposure-effect relationship of platinum salt allergy in a catalyst production plant: conclusions from a 5-year prospective cohort study. J Allergy Clin Immun 105:364–370

Messerschmidt J, Alt F, Tölg G, Angerer J, Schaller KH (1992) Adsorptive voltammetric procedure for the determination of platinum baseline levels in human body fluids. Fresenius J Anal Chem 343:391–394

Niezborala M, Garnier R (1996) Allergy to complex platinum salts: a historical prospective cohort study. Occup Environ Med 53:252–257

Nygren O, Gustavsson B, Strom L, Eriksson R, Jarneborn L, Friberg A (2002) Exposure to anti-cancer drugs during preparation and administration. Investigations of an open and a closed system. J Environ Monit 4:739–742

OSHA (2011). http://www.cdc.gov/niosh/pel88/7440-06.html

Pethran A, Schierl R, Hauff K, Grimm CH, Boos KS, Nowak D (2003) Uptake of antineoplastic agents in pharmacy and hospital personnel. Part I: monitoring of urinary concentrations. Int Arch Occup Environ Health 76:5–10

Petrucci F, Violante N, Senofonte O, Cristaudo A, Di Gregorio M (2005) Biomonitoring of a worker population exposed to platinum dust in a catalyst production plant. Occup Environ Med 62:27–33

Rosenberg B, van Kamp L, Krigas T (1965) Inhibition of cell division in *Escherichia coli* by electrolysis products from a platinum electrode. Nature 205:698–699

Rosner G, Merget R (1999) Evaluation of the health risk of platinum emission control catalysts. In: Zereini F, Alt F (eds) Anthropogenic platinum-group-element emissions and their impact on man and environment. Springer, Verlag , pp 267–283

Sanderson BJS, Ferguson LR, Denny WA (1996) Mutagenic and carcinogenic properties of platinum-based anticancer drugs. Mutat Res 355:59–70

Schierl R, Fries HG, van de Weyer C, Fruhmann G (1998) Urinary excretion of platinum from platinum industry workers. Occup Environ Med 55:138–140

Schierl R (2001) Urinary platinum levels associated with dental gold alloys. Arch Environ Health 56(3):283–286

Schierl R, Böhlandt A, Nowak D (2009) Guidance values for surface monitoring of antineoplastic drugs in German pharmacies. Ann Occup Hyg 53:703–711

Schierl R, Novotna J, Piso P, Bohlandt A, Nowak D (2012) Low surface contamination by cis/oxaliplatin during hyperthermic intraperitoneal chemotherapy (HIPEC). Eur J Surg Oncol 38:88–94

Schierl R, Lemmer A, Böhlandt A, Friedl L, Haneder S, Nowak D (2014) Silicone implants—a possible confounder for urinary platinum background concentrations? Environ Res. doi:10.1016/j.envres.2014.04.017 (in print)

Schmaus G, Schierl R, Funck S (2002) Monitoring surface contamination by antineoplastic drugs using gas chromatography-mass spectrometry and voltammetry. Am J Health Syst Pharm 59:956–961

Schramel P, Wendler I, Lustig S (1995) Capability of ICP-MS for Pt-analysis in different matrices at ecologically relevant concentrations. Fresenius J Anal Chem 353:115–117

Sottani C, Porro B, Comelli M, Imbriani M, Minoia C (2010) An analysis to study trends in occupational exposure to antineoplastic drugs among health care workers. J Chromatogr B Analyt Technol Biomed Life Sci 878:2593–2605

Umweltbundesamt (UBA) (2003) Referenzwert für Platin im Urin. Bundesgesundheitsblatt-Gesundheitsforschung-Gesundheitsschutz 46:448–450

Venables KM, Dally MB, Nunn AJ, Stevens JF, Stephens R, Farrer N, Hunter JV, Stewart M, Hughes EG, Newman Taylor AJ (1989) Smoking and occupational allergy in workers in a platinum refinery. BMJ 299:939–941

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