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Clare L.S. Wiseman *Editors*

Platinum Metals in the Environment

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Platinum Metals in the Environment

 Springer

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ISSN 1431-6250

ISBN 978-3-662-44558-7

ISBN 978-3-662-44559-4 (eBook)

DOI 10.1007/978-3-662-44559-4

Library of Congress Control Number: 2014951052

Springer Heidelberg New York Dordrecht London

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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. Romyana Djingova (Faculty of Chemistry and Pharmacy 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 Białystok, 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
Toronto, Canada

Fathi Zereini
Clare L.S. Wiseman

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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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F. Zereini and C.L.S. Wiseman (eds.), *Platinum Metals in the Environment*, Environmental Science and Engineering, DOI 10.1007/978-3-662-44559-4_1

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, NO_x 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

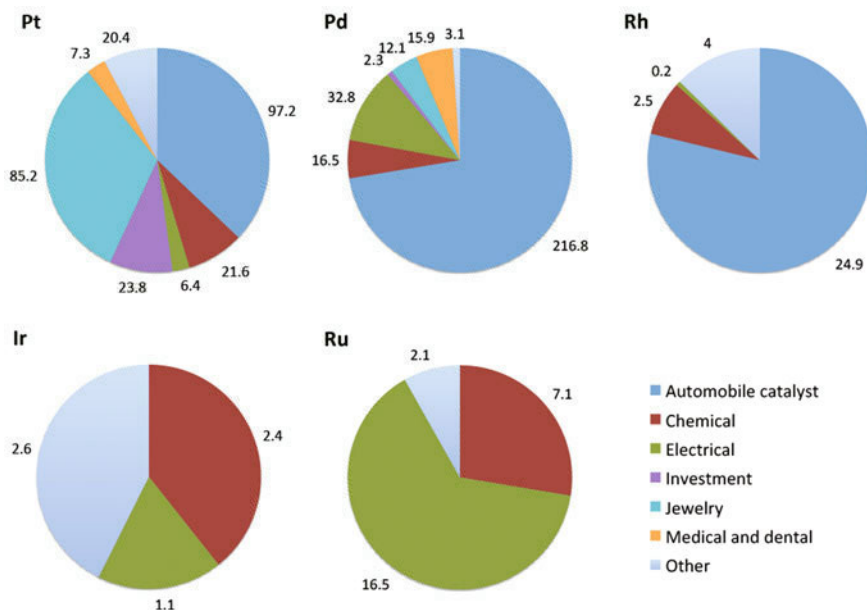


Fig. 1 Estimates of Pt, Pd, Rh, Ir and Ru demands in metric tons in different applications in 2013. Chemical applications include petrochemical and electrochemical uses. *Data source* Matthey (2013)

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 $0.5\text{--}0.8 \mu\text{g Pt km}^{-1}$. Such high emission rates are supported by estimates of Pt losses during a vehicle's lifetime, putting an upper limit on emission rates at $10 \mu\text{g km}^{-1}$ (40 % Pt loss for a mileage of 100,000 km) (Helmers 1997). Using an emission rate of $0.1\text{--}0.8 \mu\text{g Pt km}^{-1}$, 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	–	–	Helmerts (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 Garipey 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 (Helmerts 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 (Helmerts 1996; Rauch et al. 2000). More recently, the isotopic composition of Os (¹⁸⁷Os/¹⁸⁸Os) has shown that elevated PGE concentrations in urban air are associated with unradiogenic (i.e. low ¹⁸⁷Os/¹⁸⁸Os 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

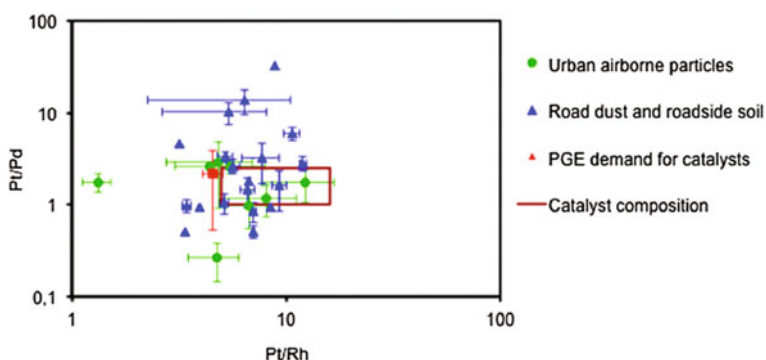


Fig. 2 Comparison of published PGE ratios (Pt/Pd vs. Pt/Rh) in road dust and roadside soils obtained in urban and roadside environments (data published in Rauch et al. 2005b) with automobile catalyst composition (Ely et al. 2001) and PGE demand for catalysts (Johnson Matthey)

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 $11\text{--}33 \text{ ng Pt L}^{-1}$ (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 (diammine[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 $<10 \text{ ng L}^{-1}$ to $3.5 \text{ } \mu\text{g L}^{-1}$. Pt is subsequently diluted in the municipal