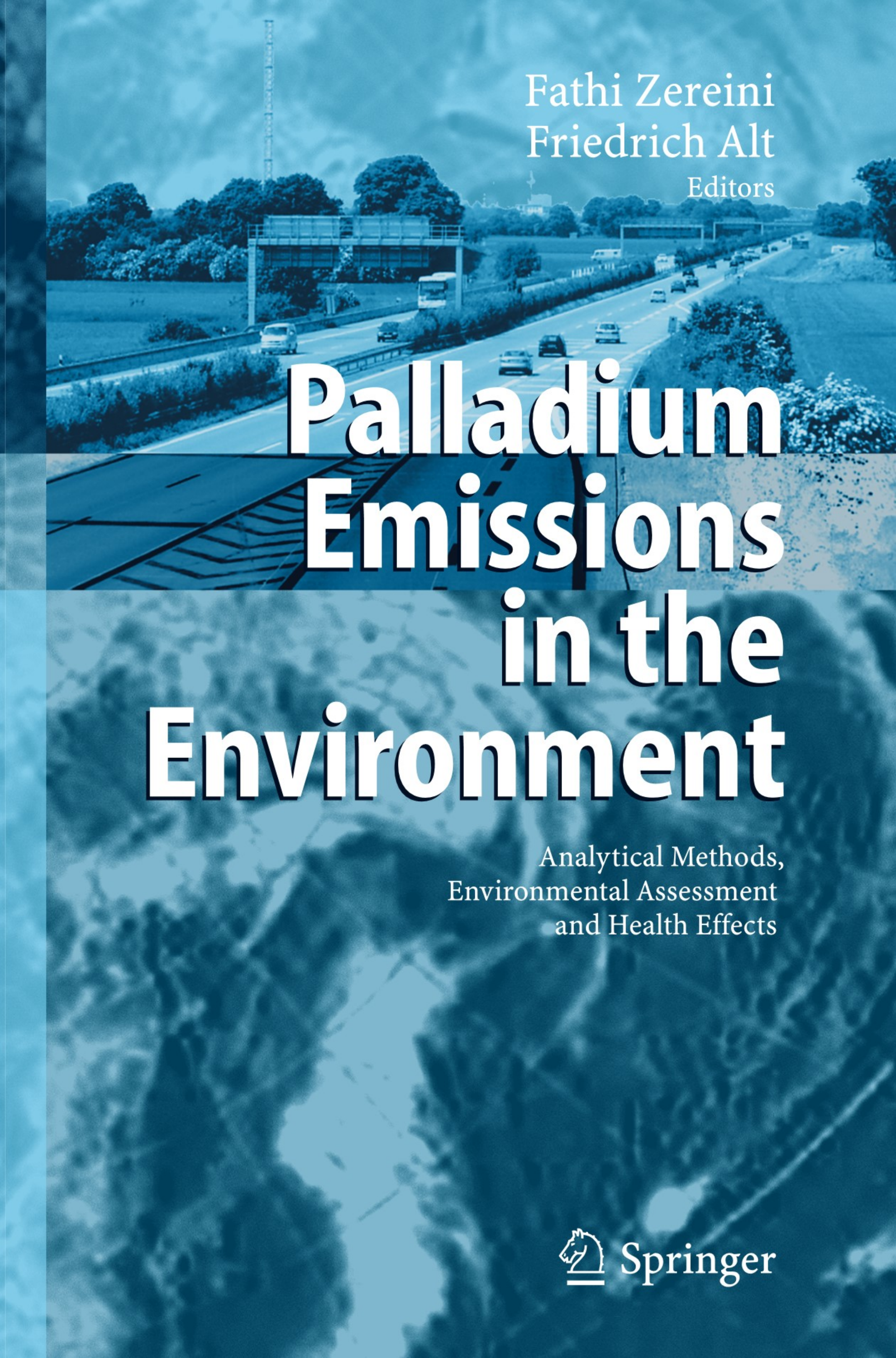

Fathi Zereini
Friedrich Alt
Editors

Palladium Emissions in the Environment

Analytical Methods,
Environmental Assessment
and Health Effects

Springer

Fathi Zereini and Friedrich Alt

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(Editors)

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Analytical Methods, Environmental Assessment and Health Effects

With 75 Figures

Springer

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Preface

In 2004 an amount of 187 tons of palladium has been sold in world market. The main demands were automotive catalyst (58%), electronics (14%), jewellery (14%) and dental practises (13%). Especially, the increasing use of palladium in catalytic converters is a reason for substantial research in this field.

Emission, environmental distribution and possible health effects of platinum have been summarized detailed in two recent books "Emissionen von Platinmetallen: Analytik, Umwelt- und Gesundheitsrelevanz" and "Anthropogenic Platinum Group Emissions – Their Impact on Man and Environment" published by Springer in 1999 and 2000 (Zereini & Alt (Eds)). But there is a clear lack of information concerning palladium. It is very important to condense the present state of research findings from emission to potential health risks for the environment and humans.

Very important is the chapter about analytical determination of palladium, which shows clearly the problems of several analytical techniques. Some data published during the last decade have to be re-evaluated because of insufficient analytical techniques. Also the finding that palladium compounds are relatively soluble and mobile in environmental settings is a great issue for further investigations.

I think it is the right time for such a comprehensive book about palladium research and I am sure that readers with different scientific background like chemists, biologists, geologists medical doctors e.g. will benefit very much from reading this book.

Munich, June 2005 Dr. Rudi Schierl

Preface of the Editors

The catalytic converter industry began producing a three-way converter which contains palladium (Pd) in 1993, as an alternative to traditional platinum (Pt)-rhodium (Rh) autocatalysts. These noble metals are used to reduce hydrocarbon, carbon monoxide and nitrous oxide in automotive emissions. While more than 90% of these pollutants are eliminated from emissions with the use of autocatalysts, their use has led to increased concentrations of PGE in the environment. Such factors as elevated temperatures and vibration of the catalytic materials lead to the release of these metals to the atmosphere. Although the benefits of catalytic converters are widely recognized, their use has stimulated heated debate regarding platinum group elements (PGE), PGE emissions and the potential risks they pose to humans and the environment. This has been fuelled by studies in occupational medicine that indicate that certain Pt metal compounds (soluble Pt metal salts) can be toxic at high concentrations.

The potential effects of Pt emissions were the focus of discussion in the 1990's. The books "Emissionen von Platinmetallen: Analytik, Umwelt- und Gesundheitsrelevanz" and "Anthropogenic Platinum Group Emissions – Their Impact on Man and Environment" published by Springer in 1999 and 2000 (Zereini & Alt (Eds)), respectively, were the first to comprehensively deal with the topic of PGE emissions, particularly Pt. Due to the enhanced use of Pd-containing catalytic converters in recent years, this metal has increasingly received greater attention.

Originally, Pd was not considered for use in autocatalysts by the industry in the 1980's, as it is not as stable as Pt and is more susceptible to contamination by impurities contained in emissions. As a consequence of technical improvements, as well as economic influences, Pd has been increasingly used in place of Pt. At present, attempts are being made by the industry to also use Pd as in catalytic converters for diesel-fuelled autos. The use of Pd in catalytic converters is seen more critically than Pt in toxicological terms, as metallic Pd has been demonstrated to cause contact allergies at high concentrations. Palladium also appears to be the most mobile of all PGE in the environment. Relative to Pt, soluble forms of Pd are taken up in considerably greater amounts by plants and aquatic organisms. Further, Pd is used in larger concentrations in catalytic converters (up to 5 g Pd per 1 liter catalyst volume) compared to Pt.

Palladium use by the catalytic converter industry in Europe increased 11-fold between 1993 and 2003, from 3.6 t to 39.8 t, since the introduction of Pd-containing exhaust converters (Johnson Matthey Platinum 1996, 2004). A total of 113.5 t Pd were employed in catalytic converters worldwide in 2004. Palladium concentrations in all environmental compartments reflect increases in the use of this metal.

In addition to autocatalysts, primary Pd deposits and the chemical and Pd-processing industries also contribute to the global distribution of Pd in the atmosphere, as will be discussed in the first chapter of this book. The mining industry in South Africa and North America has almost doubled its supply of Pd since the introduction of Pd-containing catalytic converters. Thus far, there is little data available regarding this source of emissions and its contribution to increased concentrations of this metal in the environment. This important source of emissions should be considered in the debate regarding Pd and other PGE in the environment and their human health and environmental hazard potential.

This book "Palladium Emissions in the Environment: Analytical Methods, Environmental Assessment and Health Effects" is the first to comprehensively present and discuss the results of scientific research on Pd from a variety of disciplines. The chemical, biological, geochemical, atmospheric and medical aspects of Pd emissions and their effects on humans and the environment are discussed in five main chapters as follows: (1) Sources of Pd emissions, (2) Analytical methods for determination of Pd in biological and environmental materials, (3) Occurrence, chemical behaviour and fate of Pd in the environment, (4) Bioavailability and biomonitoring of Pd, and (5) Health risk potential of Pd. These chapters are further split up into 39 sections. A total of 85 individuals from Austria, Brazil, Belgium, Canada, France, Finland, Germany, Hungary, Israel, Italy, Japan, Norway, Poland, Romania, Spain, Sweden, Switzerland, UK, USA, and have made contributions to this book.

The editors would like to thank the authors and reviewers for their contributions and cooperation in terms of the successful completion of this book. Many thanks go to Dr. C. Wiseman, Prof. Dr. W. Püttmann and Prof. Dr. W. Jaeschke from the Institute for Atmospheric and Environment and Prof. Dr. J. Oelmann from the Institute of Zoology, Goethe University Frankfurt am Main for their support. We would further like to thank Dr. R. Schierl from the Institute and Clinic for Occupational and Environmental Medicine, University of Munich, Prof. Dr. D. Stüben from Institute for Mineralogy and Geochemistry, University Karlsruhe, Dr. S. Hann from the Department of Chemistry, University of Natural Resources and Applied Life Sciences, Vienna, Austria and Dr. S. Rauch from the Chalmers University of Technology, Göteburg, Sweden.

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Frankfurt am Main, Herdecke, June 2005

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and
Dr. Friedrich Alt

Contents

1 Sources of Palladium Emissions 1

2 Analytical Methods for Determination of Palladium in Biological and Environmental Materials 71

3 Occurrence, Chemical Behaviour and Fate of Palladium in the Environment 293

4 Bioavailability and Biomonitoring of Palladium 487

5 Health Risk Potential of Palladium 549

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1 Sources of Palladium Emissions

Along with platinum (Pt), rhodium (Rh), ruthenium (Ru), Iridium (Ir) and Osmium (Os), palladium (Pd) belongs to the platinum group elements. These metals normally occur in small concentrations under natural conditions. Palladium is present in the continental crust at concentrations of 0.4 µg/kg on average. High concentrations of PGE may occur locally as a result of certain geochemical processes, resulting in amounts of as much as 10 g/tonne rock. Such economically interesting deposits contain at least 1000 times as much PGE than that measured for background concentrations. Depending on the geographical location, the infrastructure at hand and the market conditions, it is economically feasible to mine deposits of about 3 mg/kg.

Chapter 1 contains four sections which deal with the topic of Pd emission sources. Widely recognized as a primary source of PGE emissions, automobile catalytic converters are the focus of discussion. The qualitative and quantitative determination of PGE emissions from autocatalysts has been studied using a number of different methods and Bench test experiments.

In Section 1.1 of this chapter, Böck discusses the technical aspects of automobile catalytic converters and explains the various types that have been introduced to the market. In recognition of the substantial amounts of Pd, Pt and Rh that are used to produce autocatalysts, he emphasizes the economic value of recycling PGE from used catalytic converters. The volume of Pd recovered from scrapped autocatalysts in the world climbed from 5.44 t in 1998 to 12.73 t in 2003.

Bench test experiments have already demonstrated that the mechanical stress of catalytic materials causes PGE to be emitted. Such tests allow these metals to be measured directly in exhausts from the converter. As discussed in Section 1.2 by Moldovan et al., study results show that Pd emissions are dependent upon the age of the catalytic converter, among other factors. New converters emit an average of up to 63 ng Pd/km, while older autocatalysts emit between 18 and 20 ng Pd/km. In addition, emitted Pd has been found to be considerably more soluble than Pt. This is an important factor of consideration in assessing the hazard potential of using Pd in autocatalysts.

In addition to autocatalysts, industries such as chemical production and mining are also important sources for the widespread distribution of PGE in the environment. For instance, soils close to PGE-deposits (Kola Peninsula, NW-Russia) have been found to contain elevated concentrations of Pd (Reimann & Niskavaara, Section 1.4). According to Reimann & Niskavaara, 2.2 t of Pd are emitted from the Monschegorsk mining facility Russia on an annual basis. As discussed by Böck in section 1.3, the electronic, jewellery and glass production industries are also sources of PGE emissions. Such sources must also be considered in assessing PGE emissions and their possible impacts on humans and the environment.

Zereini & Alt (Editors)

1.1 Automotive Catalysts

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1.1.1 Introduction

Control and limitation of exhaust emissions from passenger cars is predominantly carried out using three-way catalytic converters (TWCs), which catalyse the transformation of these emissions, e.g. hydrocarbons (HC), carbon monoxide (CO) and nitrogen oxides (NO_x), into more innocuous compounds like carbon dioxide (CO_2), nitrogen (N_2) and water.

As catalytic active component, TWCs contain precious metals like platinum (Pt), palladium (Pd) and rhodium (Rh), belonging to the platinum group elements (PGE).

With the spread of automotive catalysts and the development of environmental legislation (e.g. EURO phase I-V, US-EPA Tier 1-2 or California LEV I-II emission standards) the annual total demand of PGE for automotive catalysts increased continuously from 35 t in the year 1980 to 235 t in the year 2000 Expert-Verlag Renningen (Hagelüken 2001-1).

According to data from the EU commission, in 2002 approximately 16 million new passenger cars and light-duty commercial vehicles came into the european market (EU 2004).

Today, in the most cases, the life span of the catalyst reaches that of the vehicle. Because of this, in the year 2000, 1,300 t PGE of the accumulated amount, mentioned above, was still in use in vehicles with a catalyst. This amount of PGE – almost as large as 3.5 times of the annual primary production – is an important PGE source for the automobile industry for the next years (Hagelüken 2001-1).

It is recognized that these precious metals are being spread into the environment to a still unknown extent, mainly due to surface abrasion of the catalyst during car operation. The final chemical form of these elements, their transformation in the environment and the repercussions of these transformations for living organisms are of paramount importance. Furthermore it is necessary that the automobile industry is enabled to assess the extent of the pollution at an early stage in order to make improvements in catalyst technology, either by stabilising the PGE more effectively (Palacios et al. 1999).

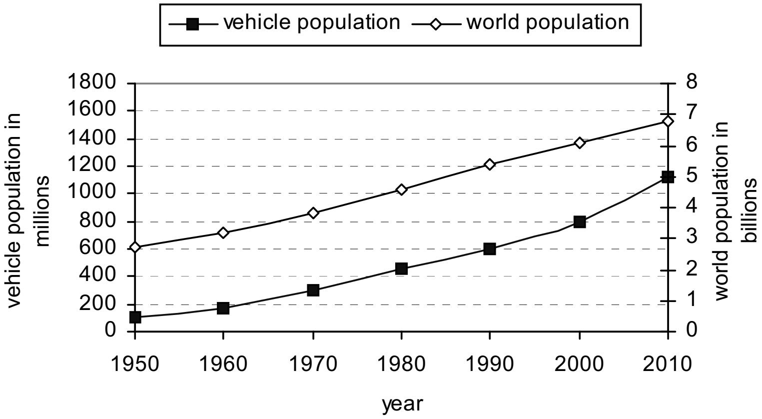

Fig. 1.1.1. Development of the world vehicle population (without motorbikes) in dependence of the increase of the world man population (after Emitec, online-published 2004)

In several studies it could be shown that PGE fine particles were co-emitted by exhaust fumes from vehicles. These particles accumulate in environmental compartiments directly close to roads, e.g. soils and plants (Zereini et al. 1993, Helmers and Mergel 1997, Lustig et al. 1997, Zereini et al. 1997, Cubelic et al. 1997, Dirksen et al. 1999, Zereini and Urban 2000). This led to the assumption that increasing platinum/palladium emissions from vehicles could also account for increasing platinum/palladium exposure of the general population. As yet no direct impact of platinum or palladium emissions from vehicles on the inner platinum/palladium exposure of the general population could be circumstantiated (MAK 2004). Nevertheless, preventing the loss of these elements into the urban environment should be a particular concern for the industrial countries.

The recycling of automobile catalysts is a profitable process, both under economical and ecological aspects. However, usual recycling processes of automotive converters lead to a verifiable release of PGE fine particles and ceramic fibre dusts (released from insulating-antivibration pads for the ceramic monolith bodies) and therefore to a exposure with carcinogenic dusts for the employees (Kuchta 2004).

For Europe, it is estimated that annually 9 till 10 millions of vehicles reach the end of their life span, with an average age of 13 till 14 years (EU 2004).

Fig. 1.1.1. shows the past and future development of the world vehicle population (without motorbikes) in dependence of the increase of the world man population.

1.1.2 Automotive catalysts

Catalysts for vehicles with petrol engine

Conventional petrol engines

An autocatalyst essentially comprises a refractory oxide support on which two or more precious metals are dispersed in very low concentrations (0.1-0.3 wt.% of the monolith). The monolith body (*honeycomb*-type) is typically made of cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) and washcoat (10-30 wt.% of corderiete), a mixture of predominantly γ-Al_2O_3 (alumina) and various proprietary base metals, to provide a high surface area film on which the catalytic component (PGE) is highly dispersed (Kim et al. 2002). The main properties required for the washcoat are the ability to be impregnated by the noble metals and to exhibit chemical inertia to reaction medium. Most of these requirements are fulfilled by using γ-Al_2O_3 (alumina) in a excess of about 90% and a mixture of rare-earth metals and/or alkaline earth metals, and other metal oxides namely CeO_2, La_2O_3, ZrO_2, BaO, TiO, Y_2O_3, NiO, WO_3, etc. The exact catalyst composition is designed by the suppliers, and generally under patent. Nowadays, combined metal oxides of three elements are being utilised as promoters of the precious metal activity in the newer generation of commercial catalysts (Palacios et al. 1999). The usual number of channels per square inch (cpsi) are about 400-600 cpsi (64-96 cells cm^{-2}) for ceramic monolith types. However, cell densities up to 900 cpsi (128 cells cm^{-2}) are now available on the market.

The characteristics of alumina that have led to it being universally accepted are (a) low cost, (b) its surface can be electrically charged either positively or negatively and, therefore, can selectively absorb ions, (c) it does not give rise to chemical reaction with the gas feed (except for some poisons), and (d) it can be shaped with accurate control of its porosity.

The functions of the base metal oxides are: (a) to stabilise the γ-$Al_2 0_3$ washcoat layer, (b) to improve dispersion of the precious metals in the washcoat thereby increasing catalytic activity, (c) to improve the thermal resistance of the whole structure, and (d) to preserve the catalyst against premature ageing, etc. (Palacios et al. 1999).

In addition to engine and exhaust system modifications, the monolithic bodies of the catalysts have also undergone changes which improve their light-off performance. Much effort has been put into the design of thin-wall, high cell density substrates that warm up faster (both ceramic and metallic) and increase the surface area available for catalytic reactions.

Likewise, catalyst formulations are being modified to improve their light-off characteristics, highly loaded Pd-only catalyst formulations representing one example of catalysts with improved light-off (Shelef et al. 2000).

Since the late eighties metallic catalyst supports are more and more available especially for medium-sized vehicles and de-luxe models. These supports were manufactured from metal foils, which consist of a FeCrAl based alloy, which contain up to 5 wt.% of aluminium (Brenscheidt 2001, Kašpar et al. 2003). A major advantage of the metallic substrate is that the wall thickness is limited by the steel rolling mill´s capabilities, not strength. Furthermore, metal monoliths show a high thermal conductivity and low heat capacity, which allow very fast heating of so-called close-coupled catalysts systems (CCCs) during the phase-in of the engine, minimising the light-off time (Kašpar et al. 2003). At present ultra high cell density metal substrates with a cell density up to 1600 psi (256 cells cm^{-2}) were developed and tested (Schaper et al. 2002, Marsh et al. 2001).

Lean-burn petrol engines (NO_x-trapping catalysts)

A major advantage of a lean burn petrol engine is the significant fuel economy. However, this engine type is not as fuel efficient as a diesel engine. In general, the exhaust emissions depend on air-to-fuel (A/F) ratio. Tuning of the engine to rich feed gives the highest power output, which, however, occurs at expenses of high fuel consumption. Under lean conditions lower combustion temperatures lead to lower NO_x emissions, however, at very high A/F ratio engine misfire occurs, leading again to high hydrocarbon (HC) emissions.

In principle there are several advantages in removing NO_x from automotive exhaust under lean conditions, i.e. A/F > 14.7, compared to the stochiometric feed (A/F = 14.7) of a traditional petrol engine, where the pullutants are abated using a TWC.

The emissions control system being developed typically involve a TCW mounted close to the exhaust manifold to control emissions during stoichiometric start-up and high speed driving, and an underfloor NO_x-trap to store NO_x during lean operation when a TWC is ineffetive for NO_x removal. The chemistry involved is shown in reactions (1)-(6).

$$NO + 0{,}5\ O_2 \rightarrow NO_2 \tag{1}$$
$$NO_2 + MCO_3 \rightarrow MNO_3 + CO_2 \tag{2}$$
$$MNO_3 + H_2 \rightarrow MO + NO + H_2O \tag{3}$$
$$2\ NO + 2\ H_2 \rightarrow N_2 + 2\ H_2O \tag{4}$$
$$MO + CO_2 \rightarrow MCO_3 \tag{5}$$

$$MCO_3 + SO_3 \quad \rightarrow \; MSO_4 + CO_2 \qquad (6)$$

NO_x is retained in the NO_x-trap as a nitrate usually derived from an alkaline earth compound (such as barium or strontium) or an alkali metal compound (such as potassium), reactions (1) and (2). Periodically the trap is exposed to short rich excursions to reduce stored NO_x to nitrogen and regnerate the trap, reaction (3) to (5). The basic materials are gradually converted to stable sulfates during prolonged use via reaction with sulfur trioxide (SO_3) derived from sulfur compounds in the fuel, reaction (6). Thus the NO_x-trap capacity must be occasionally 'desulfated', essentially the reverse of reaction (6), by treatment at higher reducing temperatures than used to reduce stored NO_x. The oxidation reaction (1) is catalysed by Pt which is also important for reaction (2) and for the nitrate decomposition, reaction (3). Rhodium is normally the catalyst for the NO_x reduction, reaction (4), and Pd may be incorparted to help oxidise HCs that inhibit reaction (1) (Twigg 2003-2).

Another advantage of lean NO_x engine is the fact that the highest exhaust temperatures are typically lower (≤ 800-850°C) compared to the stoichiometric engines (up to 1100°C). This may result in a higher catalyst durability (Kašpar et al. 2003).

In the last years several review articles were devoted to discuss new trends in automobile catalyst research and production (Shelef and McCabe 2000, Twigg 2003-1, Twigg 2003-2, Kašpar et al. 2003).

Precious metals

The choice of precious metals (synonymus to noble metals or platinum group elements) as the active catalytic material in automotive materials was the result of three factors: (a) only the precious metals had the required activity needed for the removal of the pollutants in the very short residence time dictated by the large volumetric flows of the exhaust in relation to the size of catalyst, (b) the precious metals were the only catalytic material with the requisite resistance to poisoning by residual amounts of sulfur oxides in the exhaust, (c) the precious metals were less prone to deactivation by high-temperature interaction with the insulator oxides, e.g. Al or Ce, which constitute the so-called high surface area „washcoat“ on which the active catalytic components are dispersed. The main advantages of these precious metals is that they have notable pollutant conversion activity at temperatures as low as 220°C (the usual thermal oxidation process requires temperatures in the order of 600-700°C).

Table 1.1.1. PGE compositions of modern automobile catalysts from two important manufacturers (after LAI 2002)

Manufacturer	Pt (in wt.%)	Rh (in wt.%)	Pd (in wt.%)
Engelhard	0.036	-	0.498
Engelhard	-	0.036	0.498
Degussa	0.236	0.047	-
Degussa	-	0.047	0.236

While platinum and palladium in various proportions were used as oxidation catalysts, rhodium was introduced advent of the three-way catalysts, having considerably better activity than Pt or Pd for the catalytic reduction of the oxides of nitrogen. To a large extent, the use of Pd has benefited from the significant advances made in „ oxygen storage“ materials during the 1990s. It is not uncommon to find two formulations in use on the same vehicle, e.g. Pd-only as a light-off catalyst and Pd/Rh as downstream underbody catalyst (Shelef & McCabe 2000).

For many years the classical platinum/rhodium catalyst dominated the market. In Europe the platinum and rhodium was used in a ratio of about 5:1, in the US a Pt/Rh ratio of about 10:1 was common. The continuing price increases and technical improvements stimulated the partial substituation of platinum and rhodium by palladium.

One of the first changes in technology was the substitution of Rh by Pd. Pt/Pd-catalysts were mainly used in the 1980s. At the beginning of 1990, platinum was replaced by palladium giving the Pt/Pd/Rh (with: Pt:Pd:Rh ratios from 1:14:1 to 1:28:1) and finally the Pd/Rh- and Pd-only catalysts (LAI 2002).

Older catalyts contained 0.9-2.0 g platinum and 0.1-0.4 g rhodium per 1 liter catalyst volume. New formulations work with about 0.3 g platinum and 1.5-5 g palladium at unchanged rhodium content. This means that these types of catalysts contain up to the four-fold amount of catalytically active metals in comparison to Pt/Rh-catalyst. Table 1.1.1 shows newer PGE formulations for automobile catalysts from two important manufacturer.

Catalysts for vehicles with diesel engine

Passenger cars

As with petrol engines, intensive research is being carried out to develop diesel catalyst systems for commercial or passenger cars. The success of diesel engine in Europe arises from the high power that can now be reached and also its environmentally friendly image due to low CO_2 emission derived from low fuel consumption (Palacios et al. 1999).

In 2002, over one third of all newly registered vehicles in Germany had a diesel engine. Traditionally, this share is even higher in countries such as France and Austria. The sharp increase in the number of diesel vehicles is due to their fuel economy - particular in the case of engines with direct injection systems - and comparatively low diesel prices, as well as the „fun factor". The performance, impressive torque characteristics and comfort of today's diesel vehicles make it difficult to distinguish them from comparable vehicles with a petrol engine. Above all it is because of the lower specific fuel consumption and consequently the reduced emission of the alleged greenhouse gas CO_2 – a political issue that is subject to heated debate – that the automobile industry has become interested in the diesel engine (Hosogai et al. 2003).

However, diesel engines have drawbacks such as high release of particles (soluble organic fraction, SOF) and also the release of H_2O and SO_2 giving rise to potential sulphate emission (Palacios et al. 1999).

Diesel particulate matter is suspected of causing all kinds of health problems, like asthma, persistent bronchitis, and lung cancer. Several agencies have reviewed the relevant scientific aspects, including the epidemiologic, toxicologic and experimental sides of diesel exhaust, and have proposed that diesel exhaust, or its particulate fraction, is a potential human carcinogen. Due to these facts developing of reliable catalysts (diesel exhaust treatment systems) for vehicles with diesel engines is an important challenge and necessity (van Setten et al. 2001).

Since the last years various new catalyst systems for diesel engines, such as particulate matter (PM) catalysts, hybrid catalysts and pre-turbo-charger catalysts are in development or in testing (Schaper et al. 1999, Reizig et al. 2001, Sbroglia et al. 2002, Hosogai et al. 2003, Diefke et al. 2003).

In 2000 the Peugeot 607 HDI (HDI = High Pressure Direct Injection) was the first passenger car equipped with a standard soot particle filter system. This system was developed by PSA Peugeot Citroën and called FAP (Filtre à particlues). The FAP system consists of three components: (a) a filterelement, connected with a upstream pre-catalyst and temperature- /pressure sensors, (b) a control and check system for the HDI Common-Rail-Engine, (c) vehicle integrated equipment for the addition of the fuel additiv. The main component is the particle filter, which in a first step, collects the soot particle, dispersed in the exhaust fumes. Afterwards the soot particles were combusted under use of the fuel addititve in periodic intervals (approximately every 700 km).

Tightening regulations over the the next few years will force the introduction of combined technologies for NO_x and PM (soot). Diesel engines operate very lean, and when required, Pt-based oxidation catalysts achieve control of CO and HC emissions according to following reactions (7)-(8).

$$CO + 0{,}5\ O_2 \rightarrow CO_2 \tag{7}$$

$$HC + O_2 \rightarrow CO_2 + H_2O \tag{8}$$

Modern platinum catalysts for diesel cars have been formulated to cope with both the low-temperature operation resulting from the the good fuel economy of diesel engines and, to some extent, with the effects of sulfur oxides derived from sulfur compounds in the diesel fuel.

Diesel engine PM is aggregated carbon particles with a variety of adsorbed HCs and partially oxidised organic compounds, together with water, and sulfuric and nitric acids. Several kinds of filter can trap PM, but then the problem lies in removing the trapped PM - by oxidation to harmless CO_2 and water - to prevent excess pressure drop building-up across the filter. Diesel PM burns in air above about 550°C (reaction 9), a significantly higher temperature than that of normal diesel exhaust gas (Twigg 2003-2).

$$PM + O_2 \rightarrow CO_2 + H_2O \tag{9}$$

$$NO + 0{,}5\ O_2 \rightarrow NO_2 \tag{10}$$

Several approaches have been used to remove the collected PM, such as using fuel additives to lower the combustion temperature, and including devices to increase the gas temperature. Heating devices have not been totally successful because the temperature rise from the exothermic PM combustion, if not controlled, can push the temperature in the filter to above its melting point.

One successful approach has been to combust the trapped PM with nitrogen dioxide (NO_2). The combustion occurs at temperatures as low as 250°C. The NO_2 is obtained by oxidising NO present in the exhaust gas over a Pt oxidation catalyst, reaction (10). The reaction is inhibited by SO_2, so low sulfur fuel is needed for efficient operation. Under appropriate conditions such a device - an oxidation catalyst upstream of a particulate filter - can function continuously. This is called a continuosly regenerating trap (CRT©) (Twigg 2003-2).

Usually platinum is the first choice for diesel oxidation catalysts. But recent developments in catalyst research indicate that a partial substitution of platinum by palladium is possible. For example, the noble metal specialists Umicore reports about the development of a diesel catalyst whereas one fourths of the platinum content is replaced by the cheaper palladium (Umicore 2004).

Commercial vehicles

In order to comply with future legislations (e.g. EU phase V, as of 2008) on emission limits for heavy-duty diesel trucks and buses the emission of NO_x has to be reduced by 60% and the emission of soot particles by 80% in comparison to the existing emission limit.

For some heavy-duty applications NO_x emissions can be reduced by applying exhaust gas recirculation (EGR) to the engine, while also controlling PM emissions and any additional PM produced by EGR with a CRT© system. Typically the EGR-CRT System is as efficient as a CRT for HC, CO and PM reduction, and additionally lowers NO_x by 46-58%.

Future legislation requires lower NO_x emissions, but a lower NO_x/PM ratio will be less favourable for the „CRT effect-with-NO_2“ to operate. One potential solution is to recycle NO_x so it is used several times to oxidise PM. Another potential solution is to use a catalysed particulate filter with an upstream oxidation catalyst, referred to as a CCRT™ (Twigg 2003-2).

Table 1.1.2. Demand for palladium in autocatalysts (in t) (published by the Johnson Matthey company 2004)

Year	1998	2000	2002	2003
Demand				
Europe	42.02	59.08	42.61	37.63
Japan	14.92	15.86	16.17	16.80
North America	87.69	87.23	19.90	37.63
Rest of the World	6.83	13.22	16.17	15.54
Total	151.46	175.39	94.85	107.60

After comparison and testing of different technical possibilities European manufacturers of commercial vehicles came to an agreement to support mainly the selective catalytic reduction technology (SCR) to reach the guidelines of the EU IV legislation (as of 2005).

Selective catalytic reduction of NO_x can be an efficient mean to reduce NO_x. The assumed chemical reactions are given below (reaction 11-12):

$$4\,NH_3 + 4\,NO + O_2 \rightarrow 4\,N_2 + 6\,H_2O \qquad (11)$$

$$2\,NH_3 + NO + NO_2 \rightarrow 2\,N_2 + 3\,H_2O \qquad (12)$$

The European automobile industry uniformly agreed on the use of an aqueous solution of urea as reducing agent, which should be distributed unter the labelling ‘AdBlue’.

In spite of this, at present, there are three main types of exhaust gas treatment technologies in Europe in development, depending on the manufacturer. E.g. *DaimlerChrysler* is developing a selective catalytic reduction (SCR) technology, whereas an aqueous solution of urea (AdBlue) is injectet into the catalyst. A hot combustion reduces soot particle emission. Increasing NO_x emissions were converted by a catalyst with the aid of the urea containing additive AdBlue. *MAN* uses the cooled down exhaust-gas recirculation system (EGR) with a particle filter catalyst. Here the combustion temperature is reduced by the recirculated exhaust gas whereas the production of NO_x is reduced. The increasing soot particles will be eliminated by a downstream particle catalyst. *Scania* uses an EGR system with high injection pressure. The EGR system reduces the NO_x emissions, whereas extremely high injection pressures inhibit the formation of soot particles (VDI 2004).

A review of science and technology of catalytic diesel particulate filters is given by van Setten et al. (2001).

1.1.3 PGE consumption for automotive catalysts

Between 1980 and 2000, worldwide, approximately 2,000 t of PGE were cumulatively used for TWCs. Approximately 900 t of these PGE acount for Pd and Pt, about 200 t for Rh.

In the same space of time the primary production of these metals constitute to 5,600 t. The proportion of PGE for automobile catalysts reached 35% and is the demand segment for PGE (Hagelüken 2001).

Palladium

In 2003 purchases of palladium by the global autocatalyst industry improved by 13% to 107.60 t (Table 1.1.2).

Europe

European demand for palladium in autocatalysts dropped in 2003 to 37.63 t. The primary cause was a substantial fall in sales of petrol powered cars; diesel cars gained further market share and total car sales in the region weakened. Sales of petrol cars slumped by 11 per cent, falling below 8 million units for the first time in over a decade. The market share held by petrol cars in Western Europe slipped to less than 57%. With the ratio of palladium to platinum use in petrol autocatalysts close to 4:1 an average in Europe, the drop in petrol vehicle sales had a marked effect on demand for palladium.

Thrifting also had an impact on purchases of palladium by European auto makers in 2003; average palladium loadings fell by around 4 per cent across the petrol vehicle fleet as a whole as some manufacturers continued to focus on minimising their overall PGE use.

Further thrifting of palladium loadings and growth in the market share taken by diesel cars will more than offset any increase in palladium use (Platinum 2004).

Japan

Car companies in Japan purchased 16.80 t of palladium in 2003. Palladium purchases rose largely because Japanese manufacturers used little or no metal from inventories in 2003.

The underlying use of palladium in autocatalysts in 2003 slipped lower as thrifting reduced average palladium loadings modestly. Certain manufacturers plan to shift overall PGE ratios more towards palladium than platinum, whilst average loadings are forecast to edge upwards in advance of the next phase of Japanese vehicle emissions legislation, due in 2005 (Platinum 2004).

North America

North American vehicle manufacturers purchased 37.63 t of platinum in 2003 - almost double the volume bought in 2002, when demand for new metal was heavily suppressed by the use of an estimated 43.53 t of metal from inventories.

Changes in autocatalyst PGE ratios in response to the large differential between the price of platinum and palladium started to emerge in 2003, with US auto makers in the vanguard of moves to replace platinum-rhod-

Table 1.1.3. Demand for platinum in autocatalysts (in t) (published by the Johnson Matthey company 2004)

Year	1998	2000	2002	2003
Demand				
Europe	16.95	21.15	37.63	41.67
Japan	7.46	9.02	13.37	15.86
North America	24.10	19.28	17.73	27.37
Rest of the World	7.46	9.33	11.81	14.30
Total	55.97	52.67	80.54	99.20

ium catalysts with platinum-palladium-rhodium or palladium-rhodium products. That said, the process of catalyst change is evolutionary and the impact on use of palladium last year was slight (Platinum 2004).

Platinum

Purchases of platinum for use in autocatalysts increased to 99.20 t in 2003 (Table 1.1.3). A jump in purchases of platinum by North American auto makers was responsible for approximately half of this growth. The retrofitting of catalysts and particulate filters to heavy-duty diesel trucks boosted Japanese purchases of the metal, whilst rapid growth in light vehicle sales in China and India raised demand in the Rest of the World (Platinum 2004).

Europe

In 2003 purchases of platinum by auto makers in Europe increased to 41.67 t. Several factors contributed to the growth: strongly rising diesel car sales, tightening emissions legislation, and changes to the overall ratio of PGE use.

Sales of diesel cars increased by more than 5%, reaching 6.15 million vehicles, equivalent to more than 43% of total new car registrations.

The impact of rising diesel car sales on platinum demand was compounded by the imminent introduction of the next round of European emissions legislation: Euro IV standards. These will apply to 2005 vehicle models onwards (both gasoline and diesel) and mandate very substantial cuts in emissions of all pollutants but particularly NO_x, and additionally for diesels, particulate matter.

In 2003 many Euro IV compliant models were already available and the catalysts on some of these contained higher PGE loadings to meet the tougher standards. This was particularly true of the diesel sector. One strategy for achieving the new limits an NO_X is to reduce diesel engine combustion temperatures (the formation of NO_X being highly temperature dependent). This, however, results in greater levels of CO being generated, which in turn can be managed by raising catalyst platinum loadings. As elsewhere, European auto manufacturers have re-examined their current and likely future PGE use in light of the large premium that has evolved between the price of platinum and that of palladium over the last two years. Demand for PGE in 2003, however, was still being influenced by decisions to favour the use of platinum in petrol autocatalysts that were made in 2000 and 2001 when the price of palladium spiked. Consequently, a proportion of the increase in platinum demand in 2003 was due to greater use of platinum-based catalysts rather than palladium-rich formulations an certain new vehicle models (Platinum 2004).

Japan

The Japanese vehicle industry purchased 15.86 t of platinum in 2003. Much of this surge in platinum demand occurred because of the introduction of legislation to control particulate matter emissions from heavy-duty diesel vehicles operating in the Tokyo metropolitan area. The regulation set tough new limits for particulate matter emissions for all heavy-duty trucks and buses. In essence, existing vehicles that did not meet the standards had to be fitted with either on oxidation catalyst or a diesel particulate Filter (DPF), or had to be scrapped or sold outside Tokyo. Several neighbouring prefectures also introduced heavy-duty diesel retrofit rules based on the Tokyo example.

The Tokyo legislation applied from October 2003 and caused a rush to retrofit oxidation catalysts and DPF. A resulting shortage in the supply of catalyst substrates meant that the deadline for compliance was subsequently extended to January 2004. There was also a sharp increase in purchases of new, cleaner trucks as owners replaced ageing vehicles.

Short-term national regulations reducing particulate matter emissions from large trucks are due to come into effect in the autumn of 2004. These will be followed by tighter emissions regulations for all vehicles in 2005, including very stringent particulate matter and NO_X limits for heavy-duty diesels. These have already led to the launch of new truck models fitted with oxidation catalysts and/or DPF.

North America

Purchases of platinum by the US auto industry surged by 54% in 2003 to 27.37 t. A large proportion of this increase was due to the fact that US auto makers used quite substantial volumes of platinum from stocks.

Light vehicle sales in the USA surpassed most analysts´ expectations in 2003, reaching 16.7 million units, a drop of less than 1 per cent compared with 2002. Importantly, however, sales of light trucks, notably sports utility vehicles, climbed to almost 8.9 million as they continued to take market share from passenger cars. Light trucks now account for almost 54 per cent of all light vehicle sales in the USA. Because of their larger engine sizes light trucks generally require catalysts with larger volumes or higher PGE loadings than do cars.

Use of platinum-based catalyst systems also increased in the USA in 2003 as new vehicle models were launched, reflecting decisions on PGE use that were made when palladium was trading at a hefty premium to platinum. Naturally, given the reversal in the price relationship between the two metals, US auto makers are now seeking to migrate an increasing proportion of their future vehicle models to palladium-based catalysts.

Among the biggest US-based auto makers there is no uniform approach to catalyst development and PGE use. The position is further complicated by the different emissions regulations (US and federal state regulations), which began in 2004. These require a reduction in NO_x emissions of around 75% compared to existing limits, as well as cuts in hydrocarbon (HC) emissions. In some instances this led to an increase in catalyst platinum loadings in 2003 (Platinum 2004).

Rhodium

The global automobile industry purchased a total of 20.68 t of rhodium in 2003 (Table 1.1.4). Actual use of the metal in autocatalyst manufacture, however, was higher than this as certain US auto companies continued to deplete their rhodium inventories.

Table 1.1.4. Demand for rhodium in autocatalysts (in t) (published by the Johnson Matthey company 2004)

Year	1998	2000	2002	2003
Demand (worldwide)				
Total	15.02	24.66	18.63	20.68

The growth in use of rhodium in autocatalysts was greatest in the USA and Japan. Tighter emissions regulations are due to be introduced in each country (since 2004 in the USA and in 2005 in Japan), and in both cases the permissible levels of NO_x emissions will be cut substantially.

The increase in average rhodium loading levels in the USA in 2003 was also a result of the intensive platinum and palladium thrifting programmes that US car companies adopted. In many catalyst systems a small rise in the rhodium content can help to maintain emissions conversion rates when platinum or palladium loadings are reduced. This is cost-effective as rhodium is used in much smaller proportions than platinum and palladium. The advantage of using rhodium was reinforced by the fall in the price of the metal.

European auto manufacturers also increased average petrol vehicle rhodium loading levels in 2003, both to meet the Euro IV emissions standards that come into force from 2005 vehicle models onwards, and to enable thrifting of platinum and palladium (Platinum 2004).

1.1.4 Recovery of spent automobile catalysts

In 2003 about 39% of total platinum, 57% of total palladium, and 86% of total rhodium demand is now used for the production of autocatalysts (Platinum 2004). The automotive industry consumed these metals worth more than 2.2 billion dollars in 1998. The overall demand for these metals is expected to increase in the near future, especially with the introduction of low emission diesel vehicles (both passenger cars and heavy-duty vehicles with diesel engines). Despite the rapidly growing PGE demand in an autocatalyst, less than 10% of PGE from scrapped converters are currently recycled. Hence, it is necessary to develop an economic and environmental-friendly recovery process of PGE (Kim 2000).

When spent autocalyts are subjected to the recovery process, it is very important to reclaim the full amount of PGE in a spent catalyst in view of reclamation economics. In general, it is thought that the overall recovery level of PGE should be more than 95% for a profitable process with the permissable level of secondary pollution (Kim 2000).

Due to the value of the PGE metals recycling is economically viable and material recycling is already practised sucessfully. The recovered precious metals are re-used in the production of new catalysts without any decrease in quality.

The PGE demand for automotive catalysts is a driving force for the PGE market and its price development. With the expected introduction of fuel cells for the automotive sector, especially the Pt demand will increase significantly. It is estimated, that for a fuel cell car 3 to 5 times the amount of PGE is required, than for a combustion engine car, equipped with a catalytic converter. Because of this, the collection and recycling of PGM containing catalysts has to be further optimised and efficient recycling loops have to be installed (Hagelüken 2001-2).

Today, most recycled PGE from automotive catalysts derive from North America and Japan where converters have been introduced already in the 1970s. Almost every car, which is scrapped in these regions nowaday, carries a catalytic converter. The total quantity of catalytic substrate available for recycling is estimated for North America at approx. 10,000 t/a (approx. PGE-content: 10 t Pt, 5 t Pd and 1.5 t Rh) and for Japan at 2,000 t (1.9 t Pt, 1.6 t Pd and 0.4 t Rh).

Compared to North America and Japan, the European auto catalyst recycling market is small. At 1999 the total quantity from srap catalyst recycling is estimated to 800 t catalyst substrate containing 1.0 t Pt, 0.5 t Pd and 0.2 t Rh. However, with 170 million cars registered in the EU (total Europe: 230 million) Europe will gain more significance for auto catatylst recycling in the next years (Hagelüken 2001-2).

Besides the economical aspect recycling of automotive catalyts has significant ecological benefits. For the extraction of 1 kg of platinum group elements in a South Africa Mine 150 t of ore have to be mined underground. They are hoisted vertically more than 1,000 m to the surface where they are finely milled, concentrated by flotation and subsequently pyromet-

Table 1.1.5. Recovery of palladium from recycled autocatalysts (in t) (published by the Johnson Matthey company 2004)

Year	1998	2000	2002	2003
Demand				
Europe	0.15	0.47	1.40	2.17
Japan	1.56	1.56	1.24	1.24
North America	3.58	4.82	8.08	8.39
Rest of the World	0.15	0.31	0.78	0.93
Total	5.44	7.16	11.50	12.73

allurgical processed. During this process, almost 400 t of tailings and slags occur (per 1 kg of PGE) which have to be deposited. This implies a considerable effect on nature as well as high-energy requirements.

Compared to this, the precious metal concentration in an auto catalyst (1 kg PGE per 2 t of converter respectively per 500 kg of ceramic substrate) is high and processing is more simple (Hagelüken 2001-2).

Main process technologies for the recovery of PGE can be categorised as follows: (a) hydrometallurgical or solution extraction, (b) pyrometallurgical, and (c) gasphase volatilization or selective chlorination processes.

Several review articles were devoted to discuss these recovery processes (D`Aniello 1982; Dhara 1983, Hoffmann 1988; Mishra et al. 1993, Kim 2000, Hagelüken 2001).

Palladium

The volume of palladium recovered from scrapped autocatalysts climbed to 12.73 t in 2003 (Table 1.1.5). As with platinum, the growth in the rate of recovery was greatest in Europe as the percentage of scrapped cars fitted with catalytic converters increased and greater efforts were made to remove and recycle catalysts.

The rise in the rate of recovery of palladium from autocatalysts in North America, where the auto recycling industry is more mature, was far more modest. A substantial increase, however, is forecast for 2004 and beyond as greater numbers of vehicles with heavily loaded palladium catalysts (manufactured from the mid-1990s onwards) reach the end of their lives (Platinum 2004).

Table 1.1.6. Recovery of platinum from recycled autocatalysts (in t) (published by the Johnson Matthey company 2004)

Year	1998	2000	2002	2003
Demand				
Europe	0.93	1.24	2.80	3.42
Japan	2.67	1.86	1.71	1.86
North America	9.64	10.88	11.81	13.22
Rest of the World	0.31	0.63	1.24	1.56
Total	13.55	14.61	17.56	20.06

Table 1.1.7. Recovery of rhodium from recycled autocatalysts (in t) (published by the Johnson Matthey company 2004)

Year	1998	2000	2002	2003
Demand (worldwide)				
Total	1.77	2.46	3.08	3.83

Platinum

Recovery of platinum from recycled autocatalysts increased to an estimated 20.06 t in 2003 (Table 1.1.6). Improvements in catalyst collection and recovery rates were seen in all regions, stimulated in part by the rising platinum price. Collection rates have also been rising as competition in the sector has become more intense, with several primary PGE smelters now utilising scrapped catalyst feedstock to supplement mine concentrate feed in order to maximise smelter throughput and efficiencies.

The fastest growth in the rate of recovery occurred in Europe, where cars fitted with catalysts accounted for a higher share of all scrapped vehicles. In additon, a greater emphasis has been placed on recycling of vehicles because of the European End of Life Vehicle legislation that comes into effect in 2005. The amount of platinum recovered from cars scrapped in Europe is estimated to have reached 3.42 t in 2003.

In volume terms, however, the largest rise in recovery was in the USA, where the estimated recovery of platinum jumped to 13.22 t. This reflected higher catalyst recovery rates due to the rising platinum price and a change in the mix of PGE contained in scrapped catalysts. Recovery also increased in Japan and the Rest of the World (Platinum 2004).

Rhodium

The recovery of rhodium from scrapped autocatalysts jumped to 3,83 t in 2003 (Table 1.1.7). In common with platinum and palladium, the largest rise was seen in the USA, where the volume of rhodium recovered surged by 30 per cent. The rapid rise in the platinum price helped to boost overall collection and recycling rates for scrapped catalysts. In addition, the average rhodium content of catalysts being recycled increased, a reflection of the move towards higher rhodium loading levels that occurred during the mid-1990s as new emissions legislation (targeting NO_x in particular) was introduced (Platinum 2004).

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1.2 Release of Particulate and Acid Soluble Palladium from Catalytic Converters into the Environment

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1.2.1 Vehicle emissions

Road traffic, powered by fossil fuel combustion engines, has an important impact on the air quality which affects both the environment and human health. During the last 60 years the world vehicle fleet has increased from about 40 million vehicles to over 700 million, and it is expected to reach 920 million by the year 2010 (Guibet and Faure-Birchem, 1999). The incomplete combustion of fossil fuel inside the vehicle engine causes the emission of unburned hydrocarbons (HC), carbon monoxide (CO), nitrogen oxides (NO_X), sulphur oxides (mainly SO_2), particulates, and other compounds into the environment.

As a consequence, legislation was introduced in order to limit the emission of these undesirable compounds caused by road traffic. The US Federal Clean Air Act, prescribed in California in 1970, established the first reduction in the automobile exhaust fumes emissions from passenger cars equipped with gasoline powered engines. Similar regulations were then extended to other states and countries. The definition of emission legislation is a continuous process, and a variety of new steps are being taken worldwide to further improve the air quality. As a result, emission standards for gasoline powered engines were also extended to: (i) diesel powered engines vehicles; (ii) other exhaust gas components; and, (iii) transportation other than passenger cars (Lox and Engler, 1999). In order to respect current limits of emissions and those proposed for the next few years, catalytic converter technology has proven to be the most effective passive system for the control of vehicle emissions.

1.2.2 Catalytic converters

The typical catalytic converter consists of a monolith support housed in a stainless steel canister. A mat surrounds the monolith ensuring that it is tightly packed inside the canister at all operating temperatures.

The monolith is a honeycomb substrate, generally ceramic, but sometimes metallic, traversed by a multitude of straight channels, typically 5000 or more. The ceramic monolith is made of cordierite ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_3$) with minor amounts of substances such as Na_2O, Fe_2O_3 and CaO. The most commonly used monoliths have about 62 channels per square centimetre. The monolith is coated with a layer of finely-dispersed alumina called washcoat (Fig. 1.2.1). Normally, washcoat contains aluminium oxides, cerium oxides and zirconium oxides as major constituents. The minor constituents, such as CaO and MgO, stabilize the internal surface area of some or all of the major washcoat constituents. The washcoat layer typically has a thickness of about 10-30 μm for the walls of the support and about 100-150 μm in the corners of the support.

The catalytic reactions are carried out by Pt, Pd and/or Rh (platinum group elements, PGE) dispersed throughout the washcoat. PGE are generally introduced in the catalyst by wet chemical methods such as incipient impregnation, typically using aqueous solutions of the noble metals salts, followed by a drying step to remove the water, and then by a calcinations step to decompose the noble metals salts (Lox and Engler, 1999). The type, quantity and distribution of the PGE on the washcoat layer represent a key factor affecting the performance of the catalyst system.

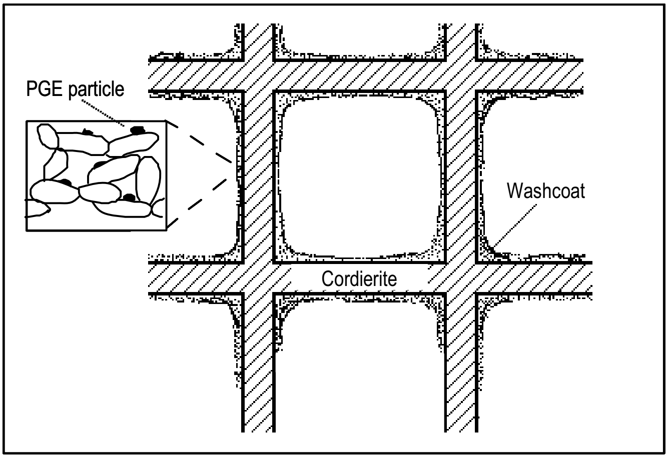

Fig. 1.2.1. Close-up view of a channel from a ceramic monolith

The chemical composition of the washcoat together with the type, quantity and distribution of the PGE on the washcoat, belong to the core know-how of the catalysts manufactures. There are numerous designs for the catalytic converter depending on the vehicle, engine and catalytic functions needed.

Gasoline catalysts

Gasoline engines, which are the most popular today, are supported by the use of three-way catalysts (TWC). Three way catalysts allow the simultaneous conversion of the three regulated species, HC, CO and NO_X into CO_2, H_2O and N_2 by maintaining the air/fuel ratio near the stoichiometric point with feedback from an oxygen sensor. Pt and Rh are involved in the oxidation of HC and CO, while Rh is used in the reduction of NO_X.

Diesel catalysts

Diesel exhaust is more complex than gasoline exhaust, and it represents all three phases of matter: gaseous, liquid and solid. Two methods are commonly used for reducing diesel emissions: diesel oxidation catalysts (DOC) and diesel particulate filters (DPF) or traps. The supports used in these applications are completely different. DPF traps particulates through a wall flow filter, ceramic filter, or ceramic foam; whereas, the role of the DOC is to reduce the soluble organic fraction (SOF), gaseous CO and HC emissions, while selectively minimizing the oxidation of SO_2 to SO_3 (H_2SO_4) (Heck and Farrauto, 2002).

DOC consists of a ceramic or a metallic monolithic support. The washcoat composition is quite different to that used for TWC. The washcoat oxides are chosen to ensure a minimal adsorption of both the soluble organic fraction and the sulphur oxides (SO_2 and SO_3).

Catalytic converter deactivation

Catalytic converter deactivation represents the loss of catalytic activity and/or selectivity over time, and is the result of a number of unwanted chemical and physical changes (Carol et al, 1989; Koltsakis and Stamatelos, 1997; Lox and Engler, 1999). The causes of deactivation could be classically divided into four categories:

Chemical:

- poisoning;
- inhibition;
- poison-induced reconstruction of catalytic surfaces; and,
- physical/chemical blockage of support pore structure;

Thermal:

- sintering;
- alloying;
- support changes;
- precious metal-base metal interactions;
- metal/metal oxide support interactions;
- oxidation;
- precious metal surface orientation; and,
- and metal volatilization.

Mechanical:

- thermal shock;
- attrition; and,
- physical breakage.

Fouling:

- coke formation.

1.2.3 Palladium

Catalytic converters are palladium's largest and fastest growing demand sector, accounting for almost 58% of total palladium demand in 2003 (Johnson Matthey, 2003).

Demand for palladium in autocatalysts started to increase significantly when clean air legislation was introduced in the United States. Moreover, in the last decade, palladium demand soared as there was a substitution from platinum to palladium in catalytic converters in the United States. This was mainly due to palladium's relatively lower cost and better performance in autocatalysts. In the last years, demand for palladium in catalysts has also shown a considerable growth in emerging countries that introduced new environmental regulations. In Europe, platinum was more widely used since it is an essential element for the more popular diesel car. However, the Belgian metal refiner Umicore recently announced that it had developed technology that will allow palladium to replace approximately 25 % of the more expensive platinum in diesel autocatalysts. Also Johnson Matthey is currently testing palladium diesel catalysts. Hence, additional Pd demand and Pd emission is foreseeable.

1.2.4 Release of PGE from autocatalysts into the environment

Nowadays it is fully accepted that automotive catalytic converters represent the major source of emission of PGE into the environment. Significant amounts of PGE are being released as a result of surface abrasion of the catalytic converter during vehicle operation. However, the number of attempts carried out in order to elucidate the real amount of released PGE and the chemical form in which they are emitted from the catalytic converter surface are very limited.

The direct determination of PGE in exhaust fumes requires an effective sampling procedure applicable to collect representative amounts of the released particles. The first studies were focussed on the release of Pt from gasoline engine catalysts (Hill and Mayer, 1977; Rosner and Hertel, 1986; König et al., 1992; Knobloch et al., 1994; Artlet et al., 2000), whereas there is little research concerning the release of Pd and Rh (Lüdke et al., 1996; Moon and Donald, 1998).

1.2.5 Quantification of particulate and acid soluble PGE released from autocatalysts in the frame of the CEPLACA project

During the period December 1997 - November 2000 the CEPLACA (1997) European research project has been running. One of the aims of this project was the study of the pathway of PGE from gasoline and diesel catalysts to the environment. Within this study, two research approaches were undertaken:

- the determination of the PGE content in car exhaust fumes under controlled ageing and European representative driving conditions;
- the study of catalyst surface changes as a function of working time and the stress to which it was subjected.

About ten catalysts, representative of 1998 European gasoline and diesel catalytic converters, were studied. The main characteristics of three of these catalysts, which will be given specific attention in this report, are shown in Table 1.2.1.

These catalysts were aged from new to 80,000 km installed in their own car following an ageing cycle that represents urban and non-urban driving conditions. Moreover, each car was checked every 10,000 km to ensure that the engine and the vehicle were in perfect condition. Exhaust fumes samples were collected directly from the car exhaust fumes pipe using a homemade device. The device was designed for passing all the raw exhaust fumes through a slightly acid absorbent solution (0.2 mol L^{-1} HNO_3) capa-

Table 1.2.1. Catalytic converters main characteristics. Adapted from (Moldovan et al., 2002), reprinted with permission. Copyright 2002. Elsevier

Catalyst type	Noble metals loading		Car/Engine
Gasoline			
catalyst A	Front: Pt/Rh 5:1	Rear: Pd/Rh 9:1	Ford Fiesta 1.3L
catalyst B	Pd/Rh 9:1	Pt pre-catalyst	Ford Fiesta 1.1L
Diesel			
catalyst C	Pt:1.29 g per catalyst		Seat Ibiza 1.9L

ble of retaining the acid soluble and particulate PGE released by the catalyst. Samples were taken following the 91441 EUDC driving cycle for light-duty vehicle testing that covers a distance of about 11 km during a time period of 20 minutes. Immediately after sampling, the sampling solution was filtered. The filtered solution contained the acid soluble PGE, the particulate fraction was retained on the filter. During the whole study, a total of 1280 particulate and acid soluble samples were collected and analysed by the five analytical laboratories involved in the project. In all cases, microwave digestion was applied to the filter, prior to analysis. Soluble PGE were analysed without pre-treatment. The analyses were performed by ICP-MS, and spectral interferences were corrected. Internal and external quality control was performed within and between laboratories. More details corresponding to the catalyst-car tandem, ageing process, sample collector, sampling conditions, sample treatment, sample mineralization and analysis are given elsewhere (Moldovan et al., 1999; Palacios et al., 2000; Moldovan et al., 2002).

Several new aspects have been taken into account within this study with respect to results found in recent literature:

- simultaneous analysis of platinum, palladium and rhodium in all exhaust fumes samples
- the sampling device allowed the differentiation between a non soluble particulate and an acid soluble PGE fraction.

Owing to the particular inhomogeneous release of PGE from the catalyst surface, the usual criteria for discarding data could not be applied. Table 1.2.2 shows the results (range, arithmetic mean, and class mean), expressed in ng km^{-1}, for the non soluble particulate and acid soluble fraction of Pd and the two other PGE released from the three different types of studied catalysts within the 30,000 to 80,000 km age range.

Table 1.2.2. Range, mean and class mean, expressed in ng km^{-1}, for non soluble particulate and the acid soluble fraction of Pd and the other two catalytic elements released from three different aged catalysts (30,000-80,000 km). Adapted from (Moldovan et al., 2002), reprinted with permission. Copyright 2002. Elsevier

	Catalyst A			Catalyst B			Catalyst C		
	Pd	Pt	Rh	Pd	Pt	Rh	Pd	Pt	Rh
Particulate									
Range	1.4 - 19.0	2.0 - 22.1	0.6 - 11.1	1.9 - 21.5	1.1 - 16.8	0.3 - 24.1	4.0 - 110.4	22.5 - 525.1	1.2 - 114.5
Mean	7.9	8.8	2.8	7.7	5.7	3.2	37.3	161.8	27.0
Class mean (0.2)	7.6	8.3	2.5	7.2	5.4	2.2	33.8	148.3	24
Soluble									
Range	nd - 44.2	nd - 1.8	nd - 15.9	0.2 - 47.7	nd - 33.9	nd - 28.6	nd - 54.9	0.3 - 53.6	0.1 - 75.8
Mean	10.6	0.5	3.4	12.7	1.1	5.6	13.7	7	7.7
Class mean (0.4)	7.5	0.4	2.2	9.8	0.4	15.9	10.6	4.6	4.8

As it can be observed from the table, although both studied gasoline catalysts are of a different type, they show a particulate Pd, Pt and Rh release that in the worst case, only differs by approximately one order of magnitude from sample to sample. The diesel catalyst, labelled as "Pt-only", released an appreciable amount of particulate Pd, and for all three PGE it shows a less uniform behaviour within the 30,000-80,000 km range than the two gasoline catalysts. The particulate Pd, Pt and Rh content in the diesel exhaust fumes is approximately two orders of magnitude higher when compared with the gasoline exhaust. The differences in washcoat composition and diesel engine running conditions could probably be the reason for this difference in behaviour.

The acid soluble Pt amount in the exhaust fumes samples from aged gasoline and diesel catalysts is significant but, in most cases, represents less than 10% of the total amount. Previous publications pointed out that the main releases of Pt into the environment from gasoline catalysts are in particulate form, and only 10% of the total Pt emissions are water soluble (König et al. 1992). Our results seem to confirm this assumption. However, this is not the case for acid soluble Pd and Rh, whose releases are about 50% higher than the non soluble particulate fraction for the gasoline catalysts. In the case of catalyst C, the soluble fraction of Pd and Rh represents about one third of the particulate fraction.

The presence of Pd and Rh in diesel exhaust fumes has been fully investigated. No risk of contamination from the sample collector or connections used was possible, since the whole sampling system was new and used only for the diesel exhaust fumes sampling. Pd and Rh presence has been confirmed by all the analytical laboratories, and moreover some laboratories checked the Rh concentration by cathodic stripping voltammetry (CSV) with analogous results.

Catalytic converter manufacturers consider the first 6400 km in the life of the catalyst as a break-in portion, and therefore not representative of the normal catalyst behaviour (Mooney, 1995). This also accounts for the PGE releases obtained in our study during approximately the first 500 km of running. Table 1.2.3 shows the results (range, arithmetic mean, and class mean), expressed in ng km^{-1}, for the particulate and acid soluble fraction of Pd and the two other PGE released from the three different types of studied

Table 1.2.3. Range, mean and class mean, expressed in ng km^{-1}, for non soluble particulate and the acid soluble fraction of Pd and the other two catalytic elements released from three different fresh catalysts (< 500 km). Adapted from (Moldovan et al., 2002), reprinted with permission. Copyright 2002. Elsevier

	Catalyst A			Catalyst B			Catalyst C		
	Pd	Pt	Rh	Pd	Pt	Rh	Pd	Pt	Rh
Particulate									
Range	22.0 - 108.0	33.2 - 313.4	10.3 - 253.0	15.5 - 132.1	15.7 - 128.3	4.4 - 33.0	4.2 - 84.4	30.8 - 406.6	6.6 - 75.4
Mean	54.2	111.5	76.9	41.6	43.2	11.7	28.1	133.0	27.6
Class mean (0.2)	54.2	111.5	76.9	41.6	43.2	11.7	28.1	133.0	27.6
Soluble									
Range	2.0 - 14.1	nd - 5.7	0.3 - 5.0	0.9 - 4.5	nd - 5.1	nd - 4.2	1.1 - 8.4	nd - 7.1	0.7 - 5.9
Mean	8.7	1.6	2.6	3.8	2.0	1.4	2.7	3.1	3.2
Class mean (0.4)	8.9	0.9	2.8	3.6	1.9	1.1	1.7	3.0	3.1

catalysts within the < 500 km age range. The exhaust fumes samples collected from the gasoline catalyst exhibit a higher and less homogeneous release of particulate fraction compared to those obtained in the 30,000-80,000 km range. The soluble fraction is in the same order. In the case of the diesel catalyst, the release is lower for the three PGE.

Scarcely any data for Pt can be obtained from the literature for comparison purposes and even less data is available for Pd (or Rh). Artelt (1997), using different engines (1.8-litre, 66-kW; 1.4-litre, 44-kW) that were running at comparable speeds showed Pt concentrations ranging from 8 to 87 ng m^{-3} that correspond to emission rates of approximately 60-87 ng km^{-1}. From the particulates collected, 33-57% had aerodynamic diameters < 10 μm, and 10-36% had diameters < 3.14 μm. In a later work, the same author (Artlet et al., 2000) studied the particulate Pt emission factor from TWCs. The data (arithmetic mean) from fresh (12-90 ng km^{-1}) and aged catalysts (9-26 ng km^{-1}) installed on a medium-powered gasoline engine (1.8-litre) showed a tendency towards decreasing Pt emission with increasing age.

Results are in good agreement with our Pt emission factor (arithmetic mean) of 111.5 ng km^{-1} for the fresh and 8.8 ng km^{-1} for the aged gasoline catalysts. No comparison can be made with particulate Pd and Rh released, because these elements were not monitored by these authors

The experimental test carried out by Inacker and Malessa (1997), with a 1.6-litre, 51-kW engine, operated under simulated stationary speed conditions, gave total observed Pt concentrations ranging from 80-110 ng m^{-3}.

Lüdke et al. (1996) collected PGEs from a standard-type three-way Pt/Pd/Rh catalyst-equipped gasoline engine running on a computer-controlled dynamometer, and concentrations of 0.3 and 120 ng m^{-3} of Pd and Pt, respectively were found.

Characterization of heavy-duty diesel vehicle emissions was performed by Lowenthal et al. (1994). There was no significant difference in the Pd emissions for trucks and buses with and without particulate traps. Palladium emission rates for PM2.5 were between 6 and 24 μg km^{-1}. However, these values are questionable since the uncertainty of the applied X-ray fluorescence analysis was very high. With the exception of the study of Lowenthal et al., nothing is known about the fraction of free palladium particles < 3μm, which would be in the respirable size range, but if one assumes that Pd particles behave similarly to Pt ones, we can conclude that palladium particles emitted from the catalytic converters are in the respirable range (EHC 226, 2002).The analysis performed in several European cities within the framework of the CEPLACA project, has shown than PGE are present in air at the respirable level (Gómez et al, 2002).

Table 1.2.4. Estimated global PGE release from gasoline and diesel passenger cars running in Madrid (Spain) and Sweden. Adapted from (Moldovan et al., 2002), reprinted with permission. Copyright 2002. Elsevier

	Palladium	Platinum	Rhodium
Madrid (Spain)			
Acid soluble (g year^{-1}) (% of the total)	160 (40)	60 (10)	80 (40)
Total (g year-1)	390	610	190
Sweden			
Fresh catalysts (g year^{-1})	828	331	169
Moderately aged catalysts (g year^{-1})	631	252	252
Total (g year^{-1})	1459	583	421

Summarising, gasoline catalysts release non soluble particulate and acid soluble PGE in the low ng km^{-1} level through their lifetime, whereas diesel catalysts release 10- to 100-fold more Pt and also appreciable amounts of Pd and Rh.

The correlation of the PGE released data with the amount of traffic could give an approximate estimation of the total emission of PGE from passenger cars. The emission data taken from this study were applied to traffic statistics from Madrid (Spain) and Sweden, and the estimated global Pt, Pd and Rh release from diesel and gasoline cars is shown in Table 1.2.4.

An interesting comparison can be made with German data, also based on engine test experiments (Kümmerer et al., 1999). A calculated amount of emitted Pt of approximately 10 kg per year for the whole of Germany can be considered to be in a range similar to that of Spain, if the figure obtained in the Madrid study is extrapolated to the whole country. Data obtained in Sweden are also in the same range, considering the low floating population of this country. However, it must be pointed out that the data presented in this chapter correspond to exhaust fumes samples collected under controlled conditions from cars having good performance. Real driving conditions are subject to uncontrolled parameters, as it is shown in Fig. 1.2.2.

Some of these factors can cause partial or complete destruction of catalyst, with consequently higher PGE release. Unpublished information from the catalyst manufacturers and automotive industry are indicative of a considerable amount of demolished catalyst (Hagelüken, 1995). The relatively

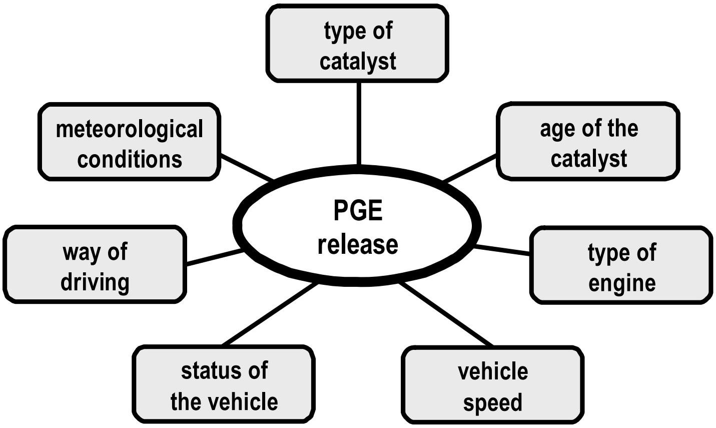

Fig. 1.2.2. Uncontrolled parameters that could affect the release of PGE from the catalyst surface to the environment

high amount of PGE found in the environmental samples (road dust, soil, plants, etc.) in comparison to the amount found in car exhaust fumes could be attributed to higher PGE release under real driving conditions.

1.2.6 Discussion about Pd emissions

Particulate Pd emissions released into the air cover a wide range for fresh gasoline catalysts and although both gasoline catalyst studied were of a different type, we could say that the particulate Pd release is in the same range: 7.9 and 7.7 ng km^{-1} for catalyst A and B, respectively. This amount can be considered very low. In fact, the investigations of Begerow el al. (1999) showed that direct exposure to traffic has not verifiable influence on the background burden of the population.

The soluble fraction represents a percentage high enough to be taken into account. This fact would have an important consequence from an environmental and toxicological point of view. Toxicological data on Pd (and Rh) are scarce. $PdCl_2$ (and $RhCl_3$) increased tumour incidences were observed in a lifetime drinking-water carcinogenicity study in mice (Schroeder and Mitchener, 1971). The allergy-eliciting potential of Pt and Pd compounds is confined to the group of ionic complexes containing halogen ligands. These halogen complexes are present in the soluble fraction of the exhaust fumes due to the high level of halogen present on the catalyst as a result of fuel additives. Furthermore the emission of soluble or volatile Pd compound as carbonyl complexes cannot be completely excluded. The solubility of Pd and Rh emitted is higher than for Pt, and therefore more adverse effects can be expected for these elements. The soluble Pd and Rh forms, which were found to be higher than expected, should be addressed in greater depth in the future. The final fate of these forms is mainly river water, in which preconcentration and bioaccumulation could lead to a biomagnification process after this type of catalyst has been in use for several decades.

The diesel catalyst differs from the gasoline catalyst with respect to the higher release of PGE. This technology should be improved, particularly when considering that the number of diesel cars with Pd as the catalytic element will substantially increase in the years to come.

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1.3 Use and Demand of Palladium for the Industry

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1.3.1 Electronic industry

Palladium for electronic components

Till some years ago the main application for platinum metal coatings was in the ornamental domain, e.g. jewellery and watches industry.

Platinum group elements (PGE) like palladium show an extraordinary chemical resistance, high hardness, high melting points and a well electrical conductivity. From there, PGE metals like palladium, platinum, ruthenium or rhodium are well suitable as anti-corrosion coatings for base metal materials. In plating technology palladium is most commonly used, followed by rhodium, platinum and ruthenium.

In recent years electroplated PGE coatings became more important in the electronic industry, e.g. Pd/Ni electroplating of connectors. Palladium coatings (e.g. Pd, Pd/Ni) were often used as alternative to hard gold layers. In this context, e.g. the *Palladium Pre-plated lead-Frame* technology (PPF) was developed. Here, palladium is used as bondable surface instead of silver. While palladium is much more expensive as silver, a cost advantage could be realised by reducing of process steps and drastically reduction of layer thickness (Simon & Yasumura 2002, Dick 2003, Freudenberger 2004).

Electrolytes for platinum metal depositions contain the respective metal in form of stable, but very different inorganic complexes. Platinum, ruthenium and rhodium will be deposited from strong acidic solutions, palladium however, predominantly from neutral or weak alkaline solutions (Gaida 1996).

Palladium demand and consumption

Purchases of palladium for the manufacture of electronic components, the second largest market for the metal in 2003, increased to 27.83 t (Table 1.3.1).

Table 1.3.1. Demand for palladium in electronics (in t) (published by the Johnson Matthey company 2004)

Year	1998	2000	2002	2003
Demand				
Europe	8.39	8.24	2.64	2.64
Japan	32.96	30.79	4.36	6.85
North America	14.30	15.08	6.53	6.68
Rest of the World	8.86	13.07	10.10	11.66
Total	64.51	67.18	23.63	27.83

As in the auto industry, however, the underlying use of palladium decreased year-on-year. The average palladium content of conductive pastes was further reduced and the miniaturisation of components continued.

The decline in consumption was due to a combination of the ongoing miniaturisation of capacitors and hybrid integrated circuits, and further thrifting of precious metal use throughout the industry. Purchases of palladium, however, by manufacturers of electronic components recovered by 18% in 2003 to 27.83 t. Multi-layer ceramic capacitors (MLCC) remain the largest electronics application for palladium (Platinum 2004).

Recycling of palladium in the plating industry (electrolytic baths)

Today precious metal recovery from dishwaters, eluates or spent eletrolytes is common in all aereas of plating by use of different technological procedures (Table 1.3.2).

In Europe, the aim of this industry is, to realise a closed loop for single production lines for the overall operation by an optimised process management and the use of modern recycling installations.

For instance, in Germany the handling and waste disposal of metal containing solutions from the surface treatment and plating industry is regulated in several orders by the WHG law (Water Resources Act).

In principle, solved metals from process solutions can be recycled as resource by suitable procedures like electrolysis, selective ion exchange or mono sludge precipitation (Gülbas 2003).

Table 1.3.2. Precious metal recovery methods used in practice (after Wingenfeld 2001).

Method	Pt	Rh	Pd	Ru
Chemical process: ion exchange	▨	▨	▨	▨
Physical process: vaporisation			▨	
Phys./chem. process: electrolysis	▨	▨	▨	▨
Combined processes: electrolysis + ion exchange			▨	
vaporisation + electrolysis			▨	

The PGE palladium, platinum and rhodium could be recovered in satisfactory quantity by electrolysis techniques. For palladium solutions, ion exchange procedures are commercially available, too. Beside the easy handling, a high loading velocity and recovery rate are the most important advantages of the ion exchange process. Because of the very strong binding of the palladium complexes, the spent adsorber resins cannot be regenerated. After incineration of the loaded resins the Pd has to be extracted by hydrometallurgical or pyrometallurgical procedures (Wingenfeld 2001).

However, there are no reliable data available about the release of PGE into the sewage water/sewage sludge by the electronic industry (e.g. companies with electroplating processes). In Germany, for instance, chemical analysis of sewage sludge indicate that for some industrialized urban areas the platinum content of the sewage sludge is predominantly due to the platinum emissions by the local industry (Lustig et al. 1997).

Recycling of palladium containing electronic scrap

There is worldwide an increasing tendency in electronics to recycle spent electrical and electronical equipment. In Europe for instance, the European Commission presses ahead the increase of recovery rates for electrical and electronical devices. The aim of these legislations is to reduce the waste from spent electrical and electronical equipment, to promote the material recycling and re-use of electrical and electronical devices and to achieve the manufacturers responsibility for the development of ecological products (EU legislations 2002/96/EG, 2003/108/EG and legislation '*Waste from Electrical and Electronic Equipment*').

A central aim of the WEEE legislation is the promotion of separate collection of spent electronics and electrical equipment by the member states. As of 2006, the member states have to realise a recycling quote of 4 kilograms for these purposes - as averaged minimum for separately collected spent devices from private households per inhabitant and year.

In common, collected electronic scrap is processed in separating works. First the electronic scrap will be controlled crushed whereas the precious metals will be extracted in high quantities by pyrometallurgical or hydrometallurgical procedures.

1.3.2 Jewellery

Palladium in the jewellery

Pure metallic palladium (Pd) has a silver-white colour. With a density of 12,02 g/cm³ and a melting point of ~1552°C palladium is the lightest respevtively the lowest melting metal of the PGE group. Because of its hardness and brittleness palladium with high finess is less used for the manufacturing of jewellery. The corrosion resistance of Pd is lower than of the other platinum metals. In comparison to pure metallic platinum with silver-white colour, palladium alloys, commonly used in jewellery, are more or less grey coloured. Following palladium alloys are used for the manufacturing of palladium jewellery: palladium 950 (designated as jeweller´s palladium, 95 wt.% Pd), palladium 750 and palladium 590. In addition palladium is used as an alloy metal for the production of whitegold (59-75 wt.% gold and 10-20 wt.% Pd).

Palladium demand and consumption

Purchases of palladium by the jewellery fabrication slipped to 10.57 t. Demand from the Japanese jewellery industry edged lower as demand for platinum alloys containing palladium fell and recycling of inventories grew. Demand from the Chinese jewellery sector also softened, with other metals increasingly used in place of palladium in white gold alloys.

Purchases of palladium for use in jewellery alloys dropped to 7.78 t in 2003 (Table 1.3.3). Japan accounted for approximately two thirds of total palladium jewellery demand.

Table 1.3.3. Demand for palladium in jewellery (in t) (published by the Johnson Matthey company 2004)

Year	1998	2000	2002	2003
Demand				
Europe	1.55	1.40	1.09	1.09
Japan	3.27	4.66	5.13	4.98
North America	0.31	0.31	0	0
Rest of the World	2.17	1.55	1.86	1.71
Total	7.30	7.92	8.08	7.78

Palladium is also a constituent of some platinum and white gold jewellery alloys produced in China, although alternatives are much more commonly used than in Japan. The fall in platinum jewellery output in China in 2003 and the increased use of metals such as nickel, zinc and tin in white gold alloys resulted in demand for palladium softening (Platinum 2004).

Recycling of palladium waste material

During the processing of solid precious metals the arising solid waste material consists predominantly of precious metals/precious metal alloys. The recycling of this waste material is a profitable process. In common, the collected PGE waste material could be well processed by precious metal smelters. The precious metals can be extracted in high quantities by e.g. pyrometallurgical or hydrometallurgical procedures.

In many european countries the emission of waste water from the production and subsequent processing of precious metals is regulated by waste legislations. In Germany, for instance, several waste water orders exist.

However, chemical examinations of sewage sludge show that in some industrial areas the jewellery (e.g. precious metals separating works, precious metal smelters) could be an important emission source for platinum group elements. Near Pforzheim city chemical analysis of sewage sludge revealed that the palladium content of the examined sewage sludge contained up to 4.7 mg palladium per 1 kg sewage sludge (LAI 2002).

1.3.3 Dentistry

Palladium in dentistry

Since the thirties of the 20th century palladium is used in dental-medically silver-palladium and gold-silver-palladium-alloys.

In Germany, for example, palladium-based alloys for the production of crowns and bridges for the primary health care were introduced in 1986 to reduce the costs for tight dental prosthesis. In the beginning of the nineties about 50-60% of the legally assured persons in Germany were provided with these Pd-based alloys (Brammertz and Aughthun 1992). However, due to the relatively high palladium metal price the production costs of Pd-based dental prothesis increased remarkably in the last 10 years.

At present about 160 palladium alloys (with palladium as main part) are commercially available. Approximately 50% of the palladium alloys are palladium-silver alloys (Pd-Ag-alloys), 25% are palladium-silver-gold alloys (Pd-Ag-Au-alloys) and about 25% are palladium-copper alloys (Pd-Cu-alloys) (DGZMK 2000).

Pd-Cu-alloys

Usually the palladium (Pd) content of palladium-copper alloys is in the range of 72-80 wt.%, the copper (Cu) content between 5 and 14 wt.%. In most cases gallium (Ga) is a further part of the Pd-Cu-alloys. Additional alloying components are gold (Au), indium (In), tin (Sn) and zinc (Zn), in uncommon cases cobalt (Co) and germanium (Ge). Partly, Pd-Cu-alloys form a multiphase texture (as many other alloys too) which could result in a raised corrodibility.

Pd-Ag-alloys

Palladium-silver alloys contain about 50-65 wt.% palladium (Pd) and approximately 20-40 wt.% silver (Ag). Further alloy metals are indium (In) and tin (Sn). In addition some alloys contain zinc (Zn) or gallium (Ga).

Pd-Ag-Au-alloys

Palladium-silver-gold alloys contain 52-78 wt.% palladium (Pd), 6-20 wt.% silver (Ag) and 4-19 wt.% gold (Au) and in addition the elements tin (Sn) and/or indium (In).

Impact of the alloy elements

The melting point of pure palladium is relatively high (~1552° C). The addition of further elements is done to reduce the high melting point of Pd, to improve the founding properties and the formation of suitable oxides for the metal-ceramic-composite. Palladium alloys show in electrochemical tests a lower corrosion resistance as gold alloys and cobalt-chromium alloys (DGZMK 2000).

Table 1.3.4. Examples of palladium based alloys as material for dental prosthesis (published in ‘Das Dental Vademekum 2004’ by BZÄK)

Compositions of Pd-based alloys for dental prosthesis (in wt.%)

Au	Pd	Ag	Pt	Cu	Sn	Zn	In	Ga
2.0	81.0	-	-	-	5.7	-	5.7	5.4
5.5	75.0	6.5	0.8	-	-	-	6.0	6.0
-	56.0	32.0	-	-	8.8	-	1.0	2.0
15.0	52.3	20.0	0.1	-	5.5	-	6.0	-
40.0	45.0	5.0	-	-	5.0	2.3	2.5	-

Table 1.3.4 shows examples of commercially available palladium alloys, which were used as material for dental prosthesis.

Palladium demand and consumption

In 2003 demand for palladium from the dental alloys market fell to 22.55 t (Table 1.3.5). Demand for palladium-based alloys had been expected to continue to recover from the recent low of 2001 in response to the fall in the price of the metal. However, in the largest market, Japan, a reduction in the level of government subsidies available for dental treatment led to a sharp drop (Platinum 2004).

Table 1.3.5. Demand for palladium in dental (in t) (published by the Johnson Matthey company 2004)

Year	1998	2000	2002	2003
Demand				
Europe	6.53	3.11	1.71	2.18
Japan	18.34	14.62	15.70	12.59
North America	12.13	7.15	6.68	7.31
Rest of the World	1.24	0.62	0.31	0.47
Total	38.24	25.50	24.40	22.55

Waste disposal of palladium in dentistry

In several European countries the release of precious metals and mercury from hospitals and medical laboratories into waste water and commercial waste is strongly regulated. In Germany, the handling and waste disposal of solutions from dental practices or laboratories, containing precious metals or mercury, is regulated in several orders by the WHG law (Water Resources Act). In principle, precious metals from waste of dental processes can be recovered by suitable procedures.

Nevertheless dentistry can be a further important palladium emission source for sewage sludge. In Germany for instance, from 1982 up to the middle of the nineties the palladium consumption in dentistry increased by the common introduction of Pd-based dental prosthesis. Chemical analysis of german urban sewage sludge showed that in the same time a significant increase of the Pd content in sewage sludge could be detected (Schuster et al. 1999, LAI 2002).

1.3.4 Chemical industry

Palladium catalysts for chemical processes

Technical catalysts were used in numerous processes in the petrol working industry, chemical production, polymerisation and in the environmental engineering.

Belonging to the catalyst type catalysts were divided into heterogeneous or homogeneous catalysts. Palladium is mainly used in heterogeneously catalysed processes.

Table 1.3.6. Pd-based heterogeneous catalysts for the production of inorganic compounds in the chemical industry (after Hassan 2003)

Process / chemical product	Catalyst	Lot size (in t/a)
Nitric acid (Ostwald process)	Pt/Rh/Pd- or Pt/Rh-gauze	475,000 (Germany, 2001)
Hydrogen peroxide (Antrachinone process)	Pd (supported or in the form of gauzes or suspensions)	217,000 (Germany, 2001)

Table 1.3.7. Pd-based heterogeneous catalysts for the production of organic compounds in the chemical industry (after Hassan 2003)

Process / chemical Product	Catalyst	Lot size (in t/a)
Caprolactame	Pd or Pt	431,000 (Germany, 2000)
Cyclohexane	Pd/Al_2O_3- or $Ni//Al_2O_3$	192,000 (Germany, 2001)
Nitrobenzene	Pd/C or Pt/C	735,000 (West Europe, 1993)
TDI (toluene diisocyanates)	Pd or Raney-Ni	150,000 (Germany, 1993)
Vinyl acetate	Pd/SiO_2	315,000 (Germany, 2001)

One important application for Pd catalysts is the technical synthesis of inorganic compounds like nitric acid or hydrogen peroxide. In Germany, these two chemical compounds were produced in a several hundred thousand tons per year benchmark (Table 1.3.6). Furthermore, Pd-based catalysts play a decisive role in the technical synthesis of basic organic compounds like acetaldehyde, caprolactame, cyclohexane, nitrobenzene, toluene diisocyanates or vinyl acetate (Tables 1.3.7-1.3.8).

Palladium demand and consumption

Purchases of palladium for use in bulk chemical manufacturing applications softened slightly in 2003, easing to 7,76 t (Table 1.3.9). Demand for palladium from the nitric acid industry improved moderately, helped by lower metal prices, but demand from the process catalyst sector fell in Europe and North America.

Table 1.3.8. Pd-based homogeneous catalyst for the production of organic compounds in the chemical industry (after Hassan 2003)

Process / chemical product	Catalyst
Acetaldehyde	$Pd(II)Cl_2$ - + $Cu(II)Cl_2$ - solution

Table 1.3.9. Demand for palladium in the chemical industry (in t) (published by the Johnson Matthey company 2004)

Year	1998	2000	2002	2003
Demand				
Europe	2.02	2.95	2.17	2.02
Japan	0.62	0.62	0.62	0.62
North America	2.17	2.02	2.33	2.17
Rest of the World	2.33	2.33	2.79	2.95
Total	7.14	7.92	7.91	7.76

The fall in price of palladium and the strong rise in the price of platinum made the use of palladium catchment gauze more cost-effective for nitirc acid producers in 2003. In addition, some manufacturers shifted from Rh/Pt catalyst alloys (5 wt.% rhodium, 95 wt.% platinum) to Pd/Rh/Pt alloys by adding of 5 wt.% palladium, (5 wt.% palladium, 5 wt.% rhodium, 90 wt.% platinum).

In the process catalyst sector, expansion of manufacturing capacity for bulk chemicals produced using palladium catalysts continued in Asia, with new vinyl acetate monomer and purified terephthalic acid plants coming on stream (Platinum 2004).

Recycling of spent PGE catalysts in the chemical industry

The fate of spent industrial catalysts is affected by legal, technical and economical factors. Legal regulations form the basic local parameters which have always to be observed. For example, these comprises the classification of spent catalysts into (a) supervision is not required, (b) supervision is required or (c) supervison is particularly required. A number of technical factors of influence affect the technical feasibility of a given recycling target. Economical factors of influence affect the benefit of the reycling and can be thus divided into monetary and qualitative factors of influence. Whereas the cost effectiveness of the recycling is determined by factors as metal price, metal content and heterogeneity of the catalyst (Hassan 2003).

Metals of the platin group elements play a decisive role in catalyst technology. Generally, spent precious metal catalysts were always recycled, with the exception of very low loaded catalysts. Priority objective is the

Table 1.3.10. Recycling methods for spent PGE-catalysts (after Hagelüken 2002)

Catalyst type	Separation-method from the support	Separation from the PGE	Rate of yield (in %)
PGE/charcoal	Combustion	From PGE-concentrates	96-99
PGE/γ-Al_2O_3	With H_2SO_4 or NaOH	From PGE-concentrates	98-99
PGE/Al_2O_3, SiO_2, ZrO_2, $BaSO_4$, $CaCO_3$	Pyrometallurgical	Use of collector metals	94-98.5
PGE-gauzes (full metal catalysts)	--	From PGE-solution	98-99
Homogeneous PGE-catalysts	Chemical separation or combustion	From PGE-concentrates	98-99

recovery of the precious metals and metals salts as basic material. For these purposes technical mature procedures like pyro- or hydrometallurgical recycling processes are available.

Table 1.3.11. Recovery rate of spent precious metal catalysts in the German chemical industry (after Hassan 2003)

Catalyst type	Recovery rate of the metal (in %)	Recovery rate of the support	Total mass of the spent catalysts (in t/a)
PGE-catalysts	> 96	very high	approx. 800
Silver-catalyts	> 93	very high	approx. 200
Total			1,000

Recycling capacities for technical catalysts exist in several industrial countries. In common, these are attached to less but highly specialised companies at few locations. Because of this, spent catalysts will be often brought to recycling across frontiers in both directions (Hassan 2003).

Table 1.3.10 gives an overview of commercial recovery methods for PGE in catalysts for the chemical industry.

An estimation of the fate and recovery rate for precious metal catalysts in the German chemical industry is given in Table 1.3.11.

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1.4 Regional Distribution of Pd, Pt and Au-Emissions from the Nickel Industry on the Kola Peninsula, NW-Russia, as Seen in Moss and Humus Samples

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Abstract

Palladium (Pd), Platinum (Pt) and Gold (Au) were analysed in 598 terrestrial moss and 617 O-horizon samples from a 188,000 km^2-area surrounding several plants within the Russian nickel industry on the Kola Peninsula. At the time of the survey ore from the Noril'sk deposits in Siberia, which has high concentrations of platinum group elements (PGE), was processed in the Monchegorsk smelter. In contrast, the smelter in Nikel and the ore roasting plant in Zapolyarnij processed predominantly local Pechenga ore, which has low PGE and Au-concentrations. Moss and O-horizon samples were analysed by a method using reductive co-precipitation to enrich PGE and Au prior to analysis. Unusually low detection limits could be reached (Au: 0.05 ppb, Pd 0.1 ppb and Pt 0.3 ppb), allowing the construction of reliable regional geochemical maps. Maps and transects demonstrate the impact of the smelters on the arctic environment. Differences in the ore feed are well reflected in the emissions. Although the Kola smelters belong to the most important PGE-emitters on earth, background concentrations for all three elements are reached at a distance of less than 200 km from source. Several geogenic anomalies highlight the further exploration potential of the area for Au and PGE-deposits. Results can also be used to calculate approximate emission figures for the Monchegorsk smelter (0.1 t Au, 2.2 t Pd and 0.8 t Pt per year).

1.4.1 Introduction

Due to the lack of sufficiently sensitive analytical methods with the potential for providing representative data for statistically significant numbers of samples collected from a large area, reliable natural background concentration levels of the PGEs and Au in various terrestrial materials are still not available. For example, at present even the mean values quoted for Pd-concentrations in the bulk continental crust differ by orders of magnitude: 0.0004 mg/kg (Wedepohl 1995), 0.015 mg/kg (Lide 1996) and 0.001 mg/kg (Taylor & McLennan 1995). Environmental sciences, attempting to study deposition of PGEs from motor-vehicle exhausts originating from catalytic converters and other technical sources, require reliable data on background concentration levels of these elements in vegetation and soils (Barefoot 1997; Balcerzak 1997). The release of Pd to the environment from catalytic converters has increased dramatically over the last 20 years. However, due to insufficient analytical methods the natural background of these elements in various sample materials like moss and soils was never established before these elements started to be released to the environment on a continental scale from car-exhausts.

The reliable determination of Au and platinum group elements (PGE) occurring in extremely low concentrations in terrestrial materials has thus become a major challenge for environmental studies as well as for geochemical (Wilhelm *et al.* 1997) and biogeochemical exploration (Dunn 1986; Kovalevskii 2001) projects. Up to now the typical result of regional scale studies, including background areas, have been data sets where often more than 90 % of all samples returned values below the detection limit. Studies near major highways or industrial emitters on the other hand, cannot provide background values.

Using an analytical technique providing extraordinarily low detection limits for Pd, Pt and Au we will demonstrate that it is possible to obtain a reliable estimate of background concentrations and variation of these elements in moss and O-horizon samples from a sizeable area. At the same time the regional impact of PGE and Au emissions from the Russian Ni-industry on the Kola Peninsula on the terrestrial environment is documented in geochemical maps. Geochemical profiles of Pd in moss and humus are used to estimate the maximum transport width of the atmospheric emissions from one of the largest Pd-pollution sources on earth to a point where the emissions can no longer be separated from the background variation. Furthermore, based on the obtained regional distribution and metal ratios in ore and our sample materials, it is possible to provide a rough estimate of the yearly emissions of Pd, Pt and Au from the Russian nickel industry on the Kola Peninsula.

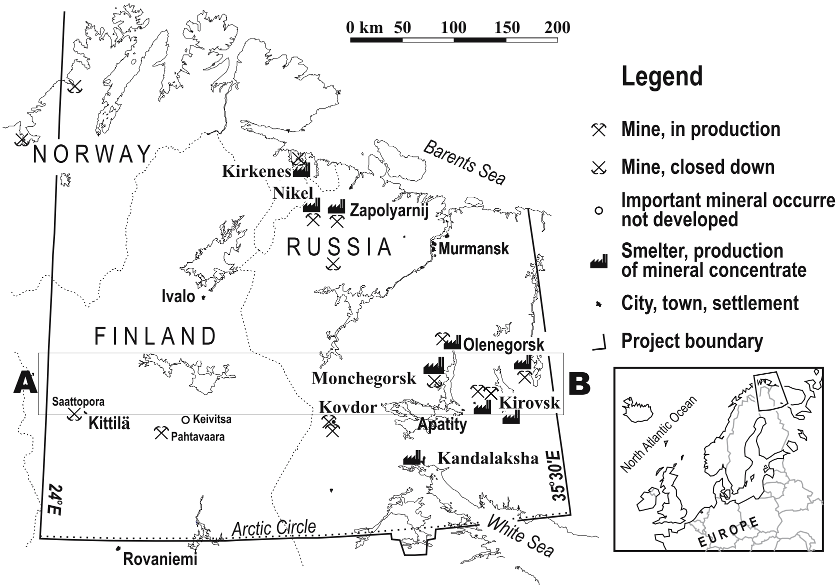

Fig. 1.4.1. Location of the survey area and of the main locations discussed in the text. The location of the east-west transect shown in Fig. 1.4.5 is marked by line A-B

1.4.2 Material and Methods

The survey area

From 1992 to 1998 the Geological Surveys of Finland (GTK) and Norway (NGU) and the Central Kola Expedition (CKE), Russia, carried out a large, international multi-medium, multi-element geochemical mapping project, covering 188,000 km^2 (Reimann et al. 1998). The entire area north of the Arctic Circle between 24^o and 35.5^o east and north to the Barents Sea (Fig. 1.4.1) was covered by the project.

With the nickel refinery at Monchegorsk, the nickel smelter at Nikel and the Cu-Ni ore roasting plant at Zapolyarnij, three of the world's largest point-source emitters of SO_2 and heavy metals are located in the Russian part of the project area. These three sources together accounted for emissions of 300,000 t SO_2, 1900 t Ni and 1100 t Cu in 1994 (Reimann et al. 1998). Emissions of platinum group elements (PGE) or Au are not given in the official statistics. Human health studies carried out in the surroundings of the smelters so far have focused on Ni (Smith-Sivertsen et al. 1997, 1998).

Table 1.4.1. Au, Pd, Pt, Cu and Ni-concentrations in average ore from Pechenga (Naldrett and Cabri 1976) and Noril'sk (Smirnov 1977)

Element	Pechenga	Noril'sk
Au	200 ppb	1600 ppb
Pd	500 ppb	36000 ppb
Pt	600 ppb	13700 ppb
Cu	0.5 wt.-%	2.7 wt.-%
Ni	1 wt.-%	2.35 wt.-%

Two ore types are processed in the Kola smelters: local Pechenga ore, processed in Nikel and Zapolyarnij, and ore imported from the Siberian Noril'sk deposits, processed in Monchegorsk. These ores differ considerably in their composition (Table 1.4.1), the Noril'sk ores are among the richest in the world in terms of their PGE and Au contents (Boyd et al. 1998).

Judging from the composition of the ore feed and the official emission figures for Cu and Ni it must be assumed that Monchegorsk was at the time of the Kola Project one of the world's largest point source emitters of PGEs, while comparatively minor emissions of PGE and Au occurred at Nikel and Zapolyarnij. Some first results of PGE and Au-analysis from soil samples collected in a number of small catchments throughout the Kola project area are given in Boyd et al. (1997). These results backed the assumption that substantial amounts of PGE and Au are emitted at Monchegorsk.

Relative to most of Europe, the Finnish and Norwegian parts of the area are still almost pristine. Human activities are mostly limited to fishery, reindeer-herding and forestry (in the southern part of the project area). Exceptions are a now-closed, large iron ore mine and mill at Kirkenes, north Norway and some small mines. Throughout the survey area population density increases gradually from north to south. All sample sites were well removed from any road. Traffic density is very low in the area and at the time of sampling no effects of traffic related PGE-emissions in the area could be expected.

In Norway, the general landscape in the coastal areas is quite rugged and the mountains reach elevations of 700 m above sea level (a.s.l.). In Russia, in the south-western part of the Kola Peninsula, there are mountains, reaching 200 – 500 m a.s.l. Near Monchegorsk and Apatity and near the coast of the White Sea occur some higher mountains (over 1000 m a.s.l.). Topographically, large parts of the area can be characterised as highlands.

The geology of the area is complex. The bedrock of the study area includes rocks forming the basement of the Fennoscandian Shield, mostly Archaean and Palaeoproterozoic in age, autochthonous and parautochthonous cover rocks of Neoproterozoic to Silurian age, and autochthonous Archaean and Palaeoproterozoic rocks in windows within the Caledonian Orogen. The rocks in large areas of the Kola Peninsula and in eastern Finland are Archaean. The supracrustal rocks include tonalites, felsic gneisses, iron quartzites and amphibolites. The main Quaternary deposits are till and peat. There are also large areas without any regolith cover, dominated by outcrops and boulder fields.

The north-south extent of the survey area is more than 500 km at the western project border. Within this distance, three vegetation zones gradually replace each other. The southern and central parts of the area fall into the northern boreal coniferous zone. Towards the north, this zone gradually gives way to sub-arctic birch forest, followed by the sub-arctic tundra zone close to the coast of the Barents Sea. These changes in vegetation zones can also occur with altitude. Major characteristics of the forest ecosystems in this area are the sparseness of the tree layer, a slow growth rate and the large proportion of ground vegetation in the total biomass production.

The dominant soil-forming process in forested and treeless regions of northern Europe is podzolisation of mineral soils (Borggaard 1997). Podzols are thus the most important soil type present throughout the survey area. Soils in the area are young. Their age ranges between 5000 and 8000 years, the time of the final retreat of the Scandinavian ice sheet. A typical podzol profile consists of five main layers: the O, E, B, BC and C-horizon. The O-horizon of podzol is characterised by a low pH value. The median pH in the O-horizon of the survey area is 3.85 (Reimann et al. 1998). The O-horizon varies in thickness from < 0.5 cm to > 20 cm, the median for the survey area being 2.5 cm.

An exhaustive description of the survey area, including maps of geology, Quaternary deposits, vegetation zones, topography, climate (precipitation, wind directions, average temperature), and mineral occurrences can be found in Reimann et al. (1998).

Sampling and sample preparation

Sampling of the 188,000 km^2 area took place from July to September 1995. The average sampling density was 1 site per 300 km^2. Samples were taken at 617 sites. Depending on availability the total number of samples ranges from 598 (moss) to 617 (O-horizon). The chemical composition of moss is dominated by atmospheric input of elements, the O-horizon reflects the complex interplay between atmosphere, biosphere and lithosphere (Reimann et al. 1998). Both media can thus be used to estimate the impact of atmospheric emissions on the terrestrial environment.

Moss (N=598): Terrestrial moss, preferably the species *Hylocomium splendens*, and if it was absent *Pleurozium schreberi* were collected. Only shoots representing the previous three years' growth were taken. All moss samples were air-dried in the laboratory, carefully separated from other species and litter, and homogenised using a cutter with non-contaminating blades.

O-horizon (N=617): This was collected with a custom-built tool to facilitate and systematise sampling, and to allow easy measurement of the volume of each sample (Äyräs and Reimann 1995). Only the top 3 cm of the organic layer were taken. If the total thickness of the O-horizon was less than 3 cm, only the organic layer was sampled and the thickness was recorded on the field sheets. From 7 to 10 sub-samples were collected at each site to give a composite sample with a minimum volume of 1 liter. The field composites were air-dried in the laboratory and sieved by rubbing them by hand (with talcum-free rubber gloves) through a 2-mm nylon sieve after removing large roots and/or plant fragments.

Analysis

The samples were ashed at 600 ^{o}C, HCl and H_2O_2 were added, the samples were heated to 90 ^{o}C and after cooling HNO_3 was added. Preconcentration/ separation of the precious metals was achieved using reductive co-precipiation (Kontas et al. 1990, Niskavaara and Kontas 1990). Final analysis was carried out on a Perkin Elmer SIMAA 6000 simultaneous graphite furnace – atomic absorption spectrometer (GFAAS). Platinum was analysed in one element mode and Pd and Au were analysed in two-element mode. For a detailed description of the analytical method used and figures of merit see Niskavaara et al. (2004). The most serious problem in quality control of PGE analysis of organic materials is the lack of certified reference materials. The only available sample is a Pt-containing vegetation sample (corn leaves, Wegscheider and Zischka, 1993). This sample was analysed for Pt using our technique to assess precision and accuracy. The certified reference value of the sample is 585 ppb Pt with a standard deviation of 107 ppb; we found 565 ppb with a standard deviation of 22 ppb. On average precision for moss and O-horizon samples is $\pm$ 25 % for Au, $\pm$ 11 % for Pd and $\pm$ 22 % for Pt.

Table 1.4.2. Summary of analytical results of moss and O-horizon samples from minimum to maximum reported concentration according to percentiles. All values in ppb

	Au		Pd		Pt	
Percentile	Moss	O-hor.	Moss	O-hor.	Moss	O-hor.
MINIMUM	<0.05	<0.05	<0.1	<0.1	<0.3	<0.3
10th	0.09	0.11	0.23	<0.1	<0.3	<0.3
20th	0.12	0.16	0.31	0.16	<0.3	<0.3
25th	0.14	0.18	0.35	0.19	<0.3	<0.3
30th	0.15	0.20	0.39	0.22	<0.3	0.33
40th	0.18	0.24	0.49	0.30	<0.3	0.44
MEDIAN	0.21	0.28	0.68	0.45	<0.3	0.62
60th	0.26	0.33	0.90	0.68	0.30	0.80
70th	0.33	0.41	1.2	1.2	0.30	1.0
75th	0.38	0.46	1.4	1.7	0.30	1.2
80th	0.42	0.53	1.8	2.2	0.40	1.4
90th	0.71	0.99	3.5	6.0	0.80	2.2
95th	1.1	1.7	7.0	13.9	1.6	3.7
98th	2.2	3.5	11	35	2.6	8.1
MAXIMUM	19	42	71	656	14	218

The samples were also analysed for up to 60 further chemical elements including Co, Cu, Ni and V using a variety of analytical techniques. Details and regional distribution maps for all elements are documented in a geochemical atlas (Reimann et al. 1998). At the time of atlas production it was, however, not possible to analyse the samples for PGE and the detection limit (DL) for Au was too high to present useful results in the Kola atlas.

1.4.3 Results and Discussion

The instrumental DLs for each material and element were calculated as three times the standard deviation of blank samples analysed as unknown quality control samples (*c.* 50 replicates) during the analyses of actual sam-

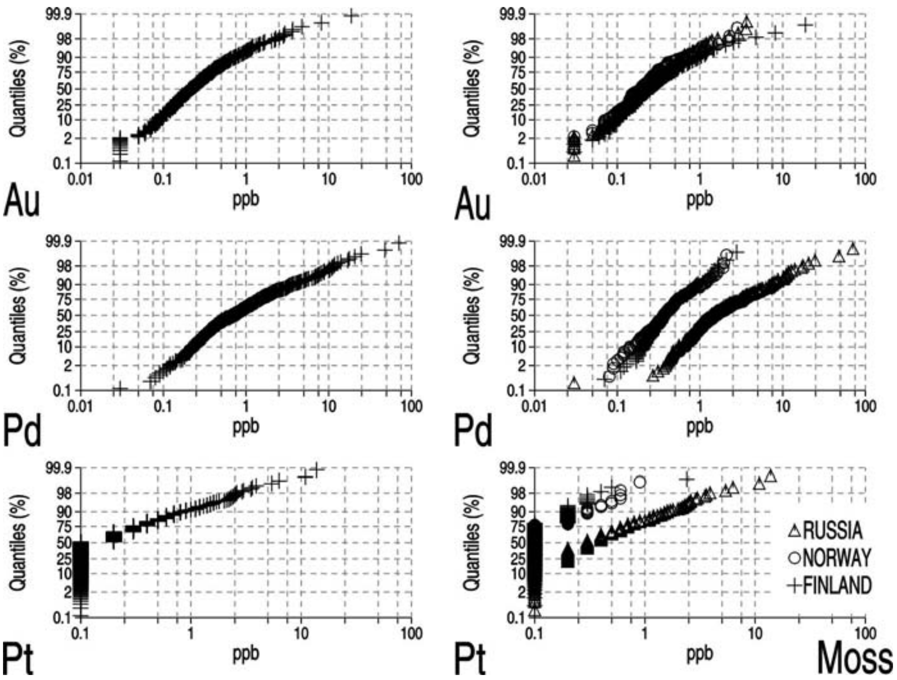

Fig. 1.4.2. CDF-diagrams of Au, Pd and Pt in moss, left hand: complete dataset, right hand: samples separated according to country of origin.

ples. DLs reached were the same for both materials (moss and O-horizon): 0.05 ppb for Au, 0.1 ppb for Pd and 0.3 ppb for Pt. Even with these low DLs some samples still returned values below the DL: Au: moss: 2% and O-horizon: 7%; Pd: moss: 1 sample and O-horizon: 10%; Pt: moss: 55 % and O-horizon: 30% of all samples (Niskavaara et al. 2004).

Table 1.4.2 summarises the analytical results for all three elements in the two sample materials according to percentiles. Median values for Au (0.21 vs. 0.28 ppb) are quite similar in moss and O-horizon, while the maximum Au-value is 2 times higher in the O-horizon. For Pd moss shows a higher median value (0.68 vs. 0.45 ppb), while the maximum value is almost 10 times higher in the O-horizon. For Pt a distinct difference between the two sample materials is visible, in moss more than 50% of all samples show values below the DL, while the median for the O-horizon is 0.62 ppb. The maximum Pt-value is about 16 times higher in the O-horizon than in moss. If calculating an anomaly/background-ratio (defined as maximum concen-

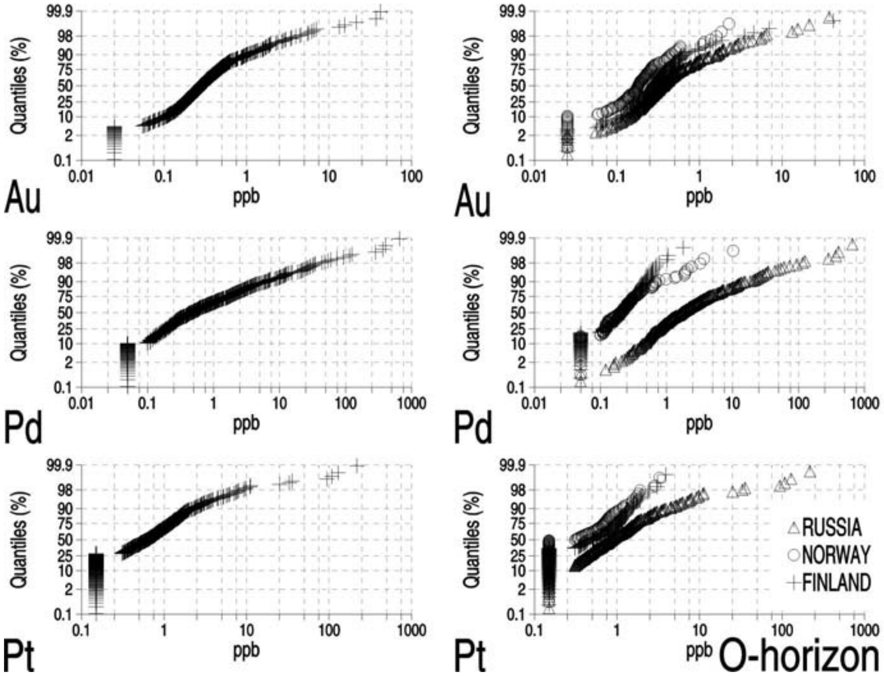

Fig. 1.4.3. CDF-diagrams of Au, Pd and Pt in the O-horizon, left hand: complete dataset, right hand: samples separated according to country of origin

tration/median) this ratio is, for all three elements, around 100 in moss (Au: 90, Pd: 104, Pt: 93) but much higher and very different in the O-horizon samples (Au: 150, Pd: 1458, Pt: 352). Thus the soil samples reflect the dominance of Pd in the Noril'sk-ore much better than the moss samples. If looking at the element ratios (Pd/Au, Pd/Pt and Pt/Au) in ore (Table 1.4.1) and moss and soil samples the soil samples give a better reflection of the ratios in the ore.

Figures 1.4.2 and 1.4.3 show cumulative probability plots (cumulative density function plots - CDF-diagrams) for the 3 elements in moss and O-horizon. On the left hand side the complete dataset is plotted, on the right hand site the three countries of origin (Finland, Norway and Russia) of the samples are used to define sample sub-sets. This allows a graphical representation of the influence of pollution on the results. Russia is the country where one could expect a major influence of contamination on the results, while Finland and Norway present almost pristine background areas. The

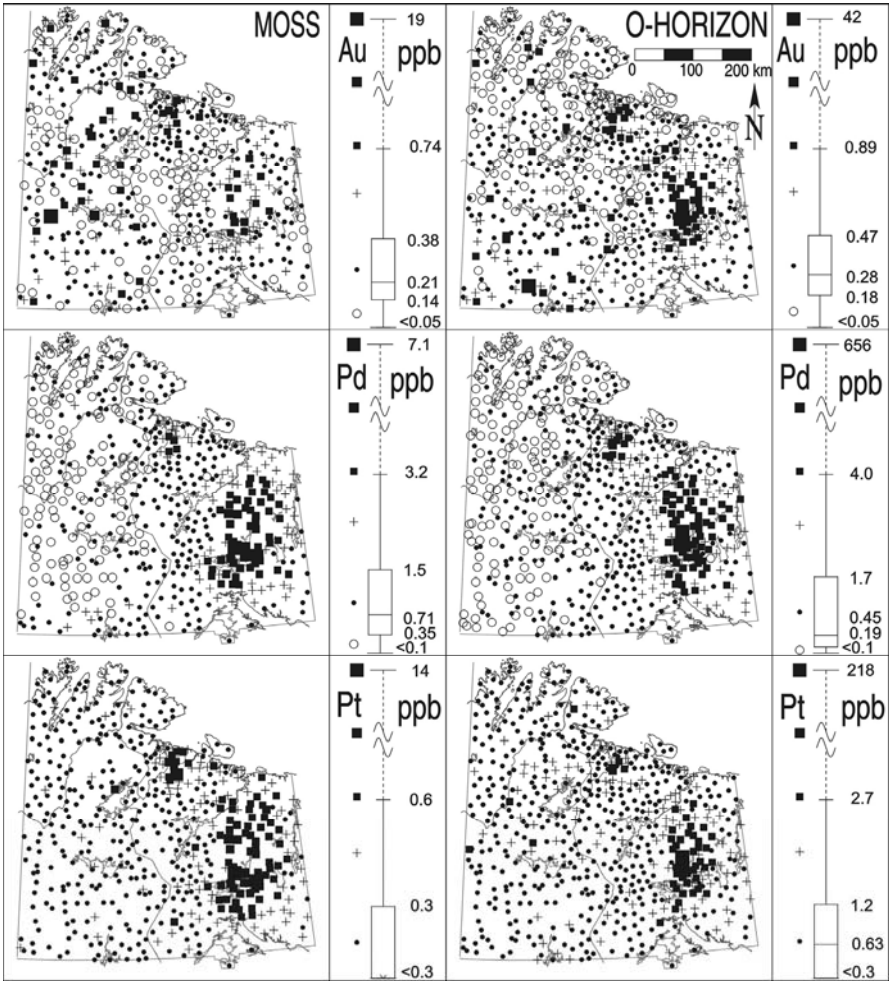

Fig. 1.4.4. Maps of the regional Au, Pd and Pt-distribution in the survey area. compare with Fig. 1.4.1 for the location of the industrial sites. Mapping techniques are detailed in Reimann et al. 1998.

vertical line at the left hand side of the diagrams results from setting samples below detection to a value of ½ of the DL and thus allows direct reading of the percentage of samples below detection from this plot.

For Au the lines for all three countries plot quite close to another in these diagrams. Surprisingly, in moss, the Finnish samples show the highest values, these must be due to the occurrence of numerous small gold showings in the Finnish survey area. Gold values in the moss would then reflect the input of geogenic atmospheric dust. For the O-horizon, the Russian samples show clearly higher Au-values than those from Finland (although the maximum values still occur in Finland). Higher values in the O-horizon than in moss can be explained by the longer accumulation time (moss: the last three years, O-horizon: at least 15 years).

For Pd and Pt the diagrams look quite different. Here a clear separation between the Russian and the Norwegian and Finnish samples is visible, the Russian samples display a considerably higher concentration range. This is especially visible in the diagram for Pd in the O-horizon, where not a single sample from Russia is below the DL. One can conclude that all samples taken in Russia contain a certain amount of Pd from the smelter emissions. For Pd there is also an interesting break in the curve for the upper 10% of the Norwegian samples. These indicate with all likelihood contamination because the smelter in Nikel is located so close to the Norwegian border (see Fig. 1.4.1).

This assumption is verified when looking at the regional distribution maps as displayed in Fig. 1.4.4. The location of the Russian nickel industry (compare with Fig. 1.4.1 for exact position) is clearly marked by all three elements.

Gold shows only a small anomaly in moss; many high values occur scattered throughout Finland. In the O-horizon the pattern is much more closely related to the location of the Russian nickel industry, although still a substantial number of high values can be observed in Finland. For all three elements the anomaly related to the Monchegorsk smelter is considerably larger than the number of high values near Nikel and Zapolyarnij. While for Au the impact of the smelters is still in the same range as the values observed in the background areas, the Pd- and Pt-anomalies are almost exclusively related to the location of the industrial sites in Russia.

Fig. 1.4.5 gives a clear impression of the relative impact of the industrial emissions on the Ni and Pd-concentrations in O-horizon and moss samples. Nickel and palladium show comparable profiles, in east-west direction background is reached in any case at less than 200 km from industry – the transport width is slightly larger in north-south direction (compare Fig.1.4. 4) because this is the main wind direction during the winter months (Reimann et al. 1998).

The differences in the ore feed (Table 1.4.1) at Monchegorsk (Pd-rich Noril'sk ore) and Nikel-Zapolyarnij (Pd-poor local Pechenga ore) can be used to separate the two sources in XY diagrams of Ni and Cu (the main elements emitted) versus Au and/or Pd (Fig. 1.4.6). The Ni-Au-diagram for

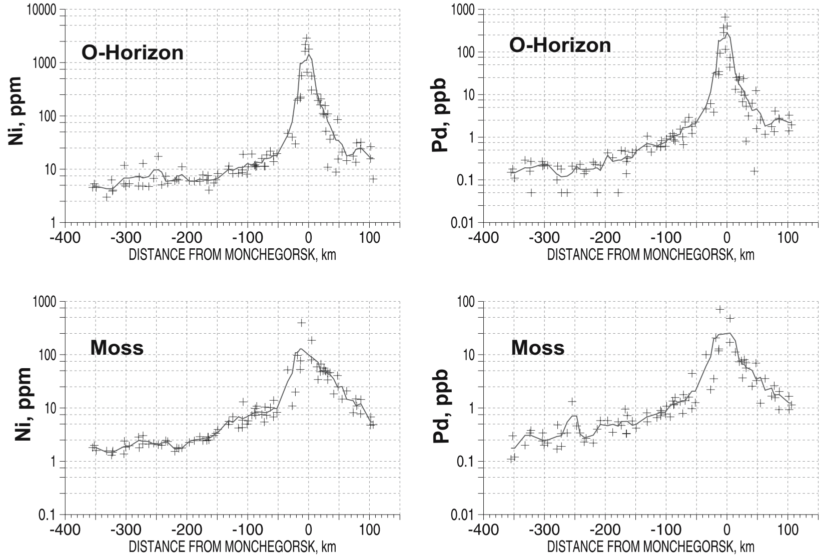

Fig. 1.4.5. Geochemical transects cutting Monchegorsk in E-W-direction (for location see Fig. 1.4.1. Ni-data from Reimann et al. (1998)

the O-horizon indicates that there are a number of samples with high Au-concentrations that cannot originate from the industrial emissions. These samples are thus of interest to the exploration geochemist.

Table 1.4.3. Background variation of Au, Pd and Pt in moss and O-horizon samples from Finland and Norway. For comparison the maximum values found near industry in Russia are also given. All values in ppb. * The Norwegian samples with Pd values up to 10.2 ppb near the Norwegian/Russian border were removed from the background data set

FINLAND/ NORWAY	Au		Pd		Pt	
	Moss	O-hor	Moss	O-hor	Moss	O-hor
MINIMUM	<0.05	<0.05	<0.1	<0.1	<0.3	<0.3
MEDIAN	0.2	0.24	0.37	0.21	<0.3	0.41
MAXIMUM	19	42	2.8	2.5*	2.4	3.9
MAXIMUM RUSSIA	3.7	37	71	656	14	218

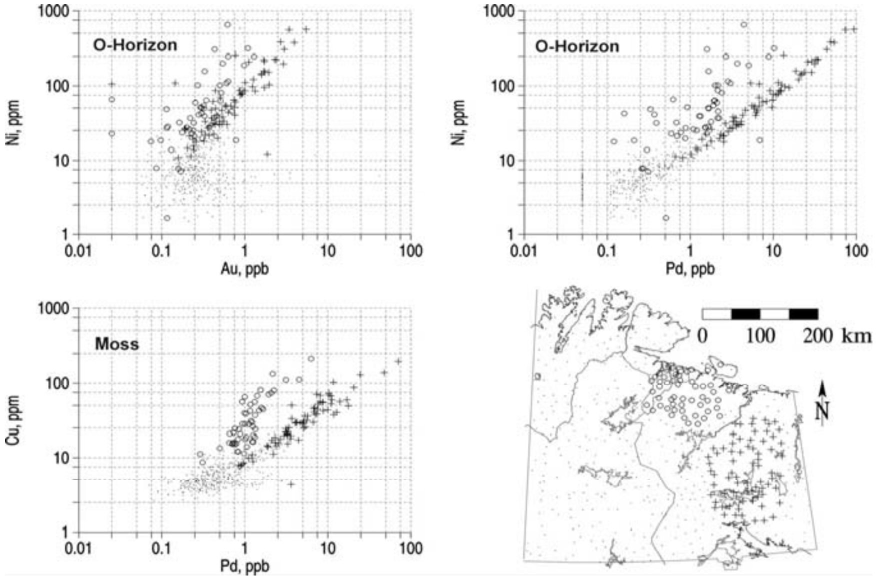

Fig. 1.4.6. XY-diagrams using Kola O-horizon and moss samples (Cu and Ni data from Reimann et al. 1998). Samples from the surroundings of Monchegorsk (crosses), Nikel-Zapolyarnij (circles) and the remainder of the survey area (dots) are marked by different symbols as indicated in the map. For exact locations of the smelters see Fig. 1.4.1.

When combining the information gathered from maps (Fig. 1.4.4), profiles (Fig. 1.4.5) and CDF-diagrams "background" (Reimann and Garrett 2005, Reimann et al. 2005) for the area can be defined as the variation seen for all three elements in moss and O-horizon in the Norwegian and Finnish samples. Table 1.4.3 summarizes the results. It is not easy to compare these results with data from other studies. We are not aware of any other investigation mapping Au, Pd, and Pt-concentrations in moss and the O-horizon at a sub-continental scale (almost 200,000 km^2 covered). Most other studies give results for urban soils (e.g. Zereini 1997, 2000, Müller and Heumann 2000, Cicchella et al. 2003) or road dust (e.g. Farago et al. 1996, Leśniewska et al. 2004). Plant materials analysed include pine needles (e.g. Dongarrá et al. 2003) and grass (e.g. Leśniewska et al. 2004) – again from urban environments, collected with the aim to demonstrate the environmental impact of traffic emissions.

Table 1.4.4. Maximum values of Au, Pd, and Pt in sample materials from this study (moss, O-horizon), Boyd et al. (1997) (Topsoil 0-5 cm), Gregurek et al. (1999) (Snow, filter residue and Monchegorsk, "Cu–Ni-Feinstein"), Noril'sk ore (see Table 1.4.1), Barnes et al. 1988 (Chondrite and Mantle) and Wedepohl (1995) (Crust). With the exception of Snow filter residue (ng l^{-1}) values for Au, Pd and Pt in ppb

Material	Au	Pd	Pt	Pt/Pd	Pd/Au
Moss	3.7	71	14	0.20	19
O-horizon	37	656	218	0.33	18
Topsoil	100	1760	466	0.26	18
Snow, filterresidue	186	2770	650	0.23	15
Monchegorsk, "Cu-Ni-Feinstein"	2539	42500	10970	0.26	17
Noril'sk ore	1600	36000	13700	0.38	23
Chondrite	152	1020	545	0.53	7
Mantle	1.2	8.3	4.4	0.53	7
Crust	2.5	0.4	0.4	1.00	0.16

Boyd et al. (1997) give data for Au, Pd and Pt in topsoils (0 – 5 cm) collected in the immediate vicinity of the Monchegorsk smelters (2 - 10 km from the smelter). They report values from 1.3 – 100 ppb Au, 4.3 – 466 ppb Pt, 39 – 1760 ppb Pd, and 0.4-13.2 ppb Rh. They demonstrated that mean and maximum values of these 4 noble metals in the topsoil reflect the composition of the Talnakh ore from Noril'sk, Siberia. Given that Boyd et al. (1997) collected a different sample material (Topsoil instead of O-horizon) much closer to the smelter their results fit well with ours. Gregurek et al. (1999) provide data for these elements in snow filter residues from the immediate surrounding of the Russian nickel industry. They found values from 3.5 - 186 ng l^{-1} Au, 33 - 2770 ng l^{-1} Pd, 11 - 650 ng l^{-1} Pt, and <0.5 - 19 ng l^{-1} Rh in snowpack samples collected at a distance of 2.5 - 8 km from the Monchegork plant. Table 1.4.4 compares maximum values from these different surveys, ore composition, and literature values for chondrite, mantle and crust and the Pt/Pd and Pd/Au ratios. The ratios give a clear indication that ore processing at the Monchegorsk plant is the source of the observed noble element concentrations.

Ore production and ore feed figures of the Russian nickel industry are approximately known (Boyd et al., 1998). In connection with the official annual emissions estimates of Cu and Ni from the smelters it is possible to give a rough estimate of the yearly Au, Pd and Pt-emissions from the Kola smelters. Assuming that the proportion of noble metals to Cu and Ni stays constant from ore to emissions, the following figures can be given for the Monchegorsk smelter, the most important source of noble metal emissions in the area: 0.10 t Au, 2.2 t Pd and 0.8 t Pt per year in the middle of the 1990ies.

1.4.4 Conclusions

Using an analytical technique with sufficiently low DL it was possible to construct reliable regional distribution maps for Au, Pd and Pt for both moss and O-horizon samples from a 188,000 km^2-area in the European Arctic. The emissions of these elements from the Russian nickel industry on the Kola Peninsula have led to the development of a sizable Au, Pd and Pt-halo surrounding the industrial sites. The data can be used to estimate yearly emissions of Au, Pd and Pt from the Monchegorsk smelter. These are approximately 0.1 t for Au, 2.2 t for Pd and 0.8 t for Pt. Still, even given some of the world's largest point source emitters of PGE, ambient background concentrations are reached at a distance of less than 200 km from these sources and the samples collected in Norway and Finland can be used to estimate background variation for these three elements in the European Arctic (Au: <0.05 – 19 ppb in moss, <0.05 – 42 ppb in O-horizon, Pd: <0.1 – 2.8 ppb in moss, <0.1 – 2.5 ppb in O-horizon and Pt <0.3 – 2.4 in moss and <0.3 – 3.9 ppb in O-horizon samples). The differences in the ore feed at Monchegorsk (Siberian Noril'sk ore) versus Nikel-Zapolyarnij (local Pechenga ore) can be used to differentiate samples from these two sources in XY-diagrams. For Au as high and even higher concentrations as those due to industrial emissions were observed at pristine background locations. These are due to geogenic sources and highlight the exploration potential of the area.

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2 Analytical Methods for Determination of Palladium in Biological and Environmental Materials

Since the introduction of Pd-containing catalytic converters, a number studies have been undertaken to determine the effects of Pd emissions on humans and the environment. This requires the development of good analytical methods to measure Pd concentrations in contaminated materials, as well as to estimate background concentrations. A direct determination of Pd using ICP-MS, for instance, is problematic, due to interfering signals and problems related to isolating this metal from the mineral matrix. Further, as Pd occurs in the environment in very small concentrations under natural conditions, it is necessary to pre-concentrate and isolate samples prior to analysis.

Despite efforts to develop methods to measure Pd in the ng/kg to pg/kg range, a standardized method for the analysis of concentrations in all important environmental media has yet to be developed. Even the latest methods such as the currently favored Isotope Dilution ICP-MS are limited. This method only yields reliable results when all possible interferences have been eliminated prior to analysis.

The choice of analytical method is dependent on the type of sample analysed and its Pd content. Presently, there are a number of different methods being used to not only analyse Pd concentrations but to pre-enrich and isolate this metal in samples. The most modern methods are not necessarily better than traditional ones; both may be used.

In this chapter, the most important analytical methods available to measure Pd in biological and environmental samples in the ng/kg to pg/kg range are presented and discussed. The focus will be on those methods which have been developed and applied by a variety of research groups. These methods primarily involve ID-ICP-MS, ICP-MS and GF-AAS, which are either used to directly measure concentrations in samples or after their pre-treatment.

Hann et al. (Section 2.1) discuss the use of ID-ICP-MS for the analysis of Pd in biological materials. For the first time, they have been able to determine background concentrations of Pd from samples of human lung. The developed method is based on a 2-step matrix separation combined with a third step involving pre-enrichment. Gomez-Gomez and Palacios-Corvillo

(Section 2.2) discuss the different separation and pre-concentration methods available and their influence on the analysis of Pd in environmental media. The advantages and disadvantages of fire assay pre-concentration, co-precipitation with tellurium (Te) and ion exchange are discussed.

In Section, Zylkiewicz & Lesniewska (Section 2.3) discuss common sources of error in the spectrometric determination of Pd in environmental samples and ways to deal with them. They conclude that trace amounts of Pd using spectrometric methods (GFAAS, ICP-MS) cannot be accurately determined without chemical pre-treatment and separation. Similarly, Pyrzynska (Section 2.6) deals with the topic of pre-concentration and separation methods for the analysis of trace amounts of Pd in environmental samples. Methods such as co-precipitation, liquid-liquid and solid phase extraction are presented and discussed. Djingova & Kovacheva (Section 2.7) demonstrate how the results obtained from analyses of Pd in various environmental media (e.g. road dust, sediments, plants) may be validated using several certified reference materials (CRMs), two separation methods and three measurement techniques (ICP-MS, ICP-AES, HPLC).

Three analytical methods to directly measure Pd in different environmental media are presented by Resano et al. (Section 2.5). These methods are solid samples-graphite furnace atomic absorption spectrometry (SS-GFAAS), solid samples-electrothermal vaporization-inductively coupled plasma mass spectrometry (SS-ETV-ICP-MS) and laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS). Figueiredo et al. (Section 2.8) describe the method nickel sulphide fire-assay and Te co-precipitation followed by ICP-MS to determine Pd concentrations in roadside soils collected from a high traffic road in Sao Paulo, Brazil. In Section 2.9, Bences et al. detail the use of graphite furnace atomic spectrometry techniques (GFAAS) to measure Pd in environmental samples. The application of GFASS for Pd after separation and pre-concentration is also discussed by Boch & Schuster (Section 2.10). New aspects regarding analytical methods to determine Pd in biological materials are discussed by Weber (Section 2.11) and Berner et al. (Section 2.12). Weber describes a method for the determination of Pd speciation in plants. Berner et al. present a procedure to the quantification of in vitro induced Pt- and Pd-DNA adducts in human lung cells. Angelone et al. (Section 2.14) conclude this chapter with a review of analytical methods to measure Pd in environmental materials.

2.1 Analysis of Palladium by High Resolution ICP-MS

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2.1.1 Introduction

As a matter of fact the impact of increasing palladium emissions is a heavily discussed issue in environmental science and medicine. The major sources for environmental Pd are PGE-based car catalyst technology (59%), dental applications (10%), and electronics (25%). The introduction of Euro Stage III legislation from January 2000 may trigger a further distribution of Pd, since the Pd-rich catalysts can best meet the imposed strict emission specifications. Although assessment and evaluation of Pd toxicology is not within the area of this chapter, it is of vital importance to stress the need for continuous monitoring of PGE exposure in terms of environmental and human bio-monitoring.

Through emission of PGE containing particulate matter (PM), palladium contaminates all important environmental compartments. Recent studies showed that Pd is the most mobile and hence bio-available of all platinum group elements (PGE) Pd>Pt>Rh (Ek et al, 2004; Jarvis et al, 2001). Environmental Pd contamination finally results in bioaccumulation of this element in the living organisms through diverse pathways. So far diverse studies could associate PGEs with several health problems in humans, e.g. asthma, nausea, increased hair loss, increased spontaneous abortion, dermatitis and others (Ravindra et al, 2004)

Generally, concentration levels of palladium in biological samples are two orders of magnitude lower than in most geological samples, i.e. below microgram per gram levels. Even in contaminated environmental samples, the concentration levels do not exceed the ng g^{-1} level. The complexity of the matrix and the low concentrations make a direct measurement of the metal extremely challenging.

Basically, palladium can be detected with any atomic spectroscopic method; however some of these methods can only deliver their full detection power when analysing samples with easy matrices (Schuster et al, 1999). Among atomic spectroscopic methods inductively coupled plasma mass spectrometry (ICP-MS) is unrivalled in terms of detection power (Bencs et al, 2003). The key features are excellent sensitivity, allowing detection limits at a sub-ng L^{-1} level in most environmental matrices, low sample consumption and high precision. However, determination of palladium by ICP-MS is not straightforward as spectral interferences impede accurate measurement. Indeed, trace analysis of palladium is still a topical research theme in the ICP-MS community.

In these specific applications, i.e. palladium analysis in environmental and biological studies, it is beneficial if not necessary to employ high resolution ICP-MS (HR-ICP-MS) rather than quadrupole ICP-MS (Q-ICP-MS), because of the enhanced sensitivity, resulting in improved detection limits (factor 50-100). With no argument, HR-ICP-MS excels Q-ICP-MS concerning elimination of spectral interferences. However, direct determination of Pd is still problematic as even the application of the high resolution setting ($m/\Delta m > 9000$) does not allow to separate all occurring interferences. Table 2.1.1 gives an overview of spectral interferences on Pd isotopes and the for separation necessary mass resolution.

Several studies accentuate the extent of spectral interferences and recommend routes either for their elimination and/or mathematical correction. Rauch et al have critically investigated the spectral interferences in road dust and river sediment samples on PGEs, using HR-ICP-MS in combination with ultrasonic nebulization (Rauch et al, 2000). Excellent limits of detection (5.3 ng L^{-1}) could be obtained exploiting the low-resolution setting of the instrument. Especially ^{105}Pd and ^{106}Pd were reported to be strongly interfered and prominent interferences could not be removed by increasing the resolution. The authors suggested mathematical correction as possible analytical strategy. A methodological study on direct ICP-MS measurement by our group showed that spectral interferences could be significantly reduced by application of membrane desolvation in combination with HR-ICP-MS (Köllensperger et al, 2000). Although oxide formation was reduced and mass resolution $m/\Delta m$ exceeded 8000, the determination of Pd in road dust was not possible without mathematical correction for Sr. Also other groups report the necessity of mathematical correction procedures, which have to be specifically designed for each sample matrix, even if the sample is less complex than road dust (i.e. urine, remote snow and ice samples) (Barbante et al, 2001; Krachler et al, 1998; Caroli et al, 2001).

Table 2.1.1. Isotope abundances and possible spectral interferences of Pd isotopes

Isotope	Abundance [%]	Interference	Abundance [%]	Required resolution [m/Δm]
^{102}Pd	1.02	$^{86}Sr^{16}O$	9.84	71700
		$^{204}Hg^{2+}$	6.85	1257
		$^{204}Pb^{2+}$	1.37	1261
		^{102}Ru	31.60	80780
^{104}Pd	11.14	$^{40}Ar\,^{64}Zn$	48.61	8300
		$^{88}Sr^{16}O$	82.36	29800
		^{104}Ru	18.70	74400
		$^{208}Pb^{2+}$	52.38	1234
^{105}Pd	22.33	$^{40}Ar\,^{65}Cu$	30.71	7042
		$^{89}Y^{16}O$	99.76	24370
		$^{88}Sr^{17}O$	0.03	330000
		$^{87}Sr^{18}O$	0.01	35260
		$^{87}Rb^{18}O$	0.01	32100
		$^{88}Sr^{16}O^{1}H$	82.37	31980
		$^{68}Zn^{37}Cl$	4.5	7320
		$^{36}Ar^{69}Ga$	0.20	92000
		$^{70}Zn^{35}Cl$	0.45	9615
		$^{35}Cl^{35}Cl^{35}Cl$	43.5	72044
^{106}Pd	27.33	$^{40}Ar\,^{66}Zn$	27.79	7033
		$^{90}Zr^{16}O$	51.34	27492
		$^{89}Y^{17}O$	0.037	58800
		$^{88}Sr^{18}O$	0.16	70600

(Part 1 of 2)

Table 2.1.1. (cont.) Isotope abundances and possible spectral interferences of Pd isotopes

Isotope	Abundance [%]	Interference	Abundance [%]	Required resolution [m/Δm]
		^{106}Cd	1.25	35468
^{108}Pd	26.46	^{40}Ar ^{68}Zn	18.72	6474
		^{38}Ar ^{70}Ge	0.014	8600
		^{92}Zr^{16}O	17.07	27386
		^{92}Mo^{16}O	15.01	49724
		^{108}Cd	0.89	369535
^{110}Pd	11.72	^{40}Ar ^{70}Ge	20.44	5927
		^{94}Mo^{16}O	9.33	21265
		^{40}Ar^{70}Zn	0.62	6300
		^{94}Zr^{16}O	17.36	27929
		^{110}Cd	12.49	50834

(Part 2 of 2)

Evidently, this analytical approach–direct measurement and mathematical correction — fails in the case of environmental biomonitoring of Pd — when a large number of samples with different matrices have to be analysed. Quality assurance in these studies would imply the assessment of each potentially interfering element for each different sample matrix, which is not applicable on a routine basis. Hence, establishment of matrix separation procedures is an absolute prerequisite for comprehensive Pd studies. Matrix separation procedures have a long tradition in PGE analysis. In the past, enrichment by pre-concentration used to be the main objective, but with the introduction of the highly sensitive ICP-MS technique the analytical background changed and selective and quantitative separation of interfering elements became important. So far most commonly ion exchange procedures were developed as PGE form negatively charged chloro-complexes (Hann et al, 2001). Both cation and anion exchange procedures could be applied. Generally, quantification in these multi-step procedures is complicated by partial loss of analyte due to incomplete elution. As a consequence, isotope dilution was propagated as method of choice to compensate for this effect. Moreover, in this way non-spectral interferences can be corrected for. Cu, Ga, Y, Sr, and Rb can be quantitatively separated via cation exchange (Whiteley and Murray, 2003; Meisel et al, 2003). As a limiting factor Zr and Mo cannot be removed effectively, especially when HF was used for digestion. Both elements form oxide interferences on most of the Pd isotopes, thus it is not possible to find two undisturbed isotopes for IDMS. For accurate analysis of Pd by IDMS, anion exchange was found to be suitable (Yi and Masuda, 1996; Jarvis et al, 1997; Rehkämper and Halliday, 1997; Müller and Heumann, 2000). However, as elution of Pd involves multiple steps utilizing highly concentrated acids, (1) cleaning of resins is labour intensive and (2) subsequent enrichment of Pd is tedious requiring an open vessel treatment to eliminate the high acid concentration in the sample. Another matrix separation/pre-concentration strategy implying selective Pd complexation (Schuster and Schwarzer, 1996) failed when applied to ICP-MS detection as the selectivity was insufficient. Nickel sulfide fire assay is the most widely used technique that combines matrix separation and pre-concentration. Although it is compatible with ICP-MS it has some disadvantages (the optimum flux composition varies with the sample matrix, it has high and variable blanks depending on the reagent purity, it has complicated and time consuming working steps, and the quality of the results depends on the experience of the analyst), which make clear that there is a need for alternative methods (Jarvis et al, 1997; Pearson and Woodland, 2000; Ely et al, 1999; Enzweiler et al, 1995; Jin and Zhu, 2000).

Focus of our work was to develop a generic approach applicable to ultratrace analysis down to sub ng g^{-1} levels in different sample matrices (biological tissue, road dust) on a routine basis. This implied the establishment of a system pre-concentrating and efficiently separating Pd from interferences for at least two Pd isotopes amenable to ID-ICP-MS. As previously discussed, only an intelligent combination of ion exchange with selective enrichment could meets these demands.

2.1.2 Experimental

Measurements were carried out using an Element 1 (Thermo Finnigan, Bremen, Germany), a high-resolution sector field mass spectrometer. As sample introduction system, a micro concentric nebulizer equipped with a membrane desolvation unit (MCN 6000AT+, Cetac Technologies Inc., Omaha, Nebraska, USA) was employed. The flow injection (FI)-system used for the pre-concentration procedure is described elsewhere in detail (Rudolph et al, 2005a).

For development and validation of the method human autopsy tissue (3 sub-samples of human lung) was provided by the Department of Forensic Medicine of the Medical University of Vienna. Preparation of the lung tissue, as well as of the road dust samples combined a two step microwave digestion followed by an open vessel treatment. A comprehensive description of the sampling procedure and sample pre-treatment can be found elsewhere (Rudolph et al, 2005b). Prior to pre-concentration, the sample solutions underwent a two step matrix separation in order to eliminate all possible spectral interferences. The first step consisted of a cation exchange procedure (AG 50W-X8) in order to eliminate the main cationic interferences such as Cu, Y, Sr and Rb. The second step followed (Eichroms Re extraction resin), eliminating the interferences not separated by the first step, such as Zr and Mo. A detailed description of the separation procedure, together with matrix elimination efficiencies is presented elsewhere (Rudolph et al, 2005a). The interference free, palladium containing sample solution was subsequently pre-concentrated using the complexing agent N,N-diethyl-N´-benzoylthiourea (DEBT) for enabling ultra trace measurements of palladium in biological samples such as body fluids and human tissue samples (Schuster and Schwarzer, 1996; Limbeck et al, 2003). In order to compensate for analyte losses and long term drifts of the instrumentation, quantification of all samples was carried out by isotope dilution analysis.

Both the matrix separation procedure and the pre-concentration procedure were validated by the certified reference material, road dust (BCR-723), due to the lack of appropriate reference material for palladium in biological tissue samples. However, it could be assumed that palladium in lung tissue samples is present in the same chemical form as in road dust. The target value of palladium in BCR-723 is 6.0 ± 1.8 ng g^{-1}. As can be seen in Table 2.1.2 our measured value agreed well with the certified value.

Table 2.1.2. Palladium in certified road dust, measured vs certified values

Sample Road dust-BCR 723	Measured value ($^{105}Pd/^{108}Pd$) [ng g^{-1}]	Certified value [ng g^{-1}]
Average	6.3 ± 2.7	6.0 ± 1.8

2.1.3 Results and Discussion

Determination of palladium in biological samples

So far, determination of platinum group elements in biological samples mainly addressed monitoring of platinum. The previously described analytical difficulties in measuring low concentrations of palladium in biological materials have led to a complete lack of comprehensive data on the baseline levels, making health risk studies on humans extremely difficult. As already mentioned general population is mainly exposed to palladium through dental alloys, skin contact with palladium-containing jewellery and emissions from automobile catalytic converters. Exposure through inhalation of palladium from automobile catalyst emissions is expected to be in the low ng g^{-1} range per day. The exposure was estimated to be factor of 5 lower compared to Pt exposure. A recent study by our work group, showed platinum concentrations ranging between 0.03 and 0.78 ng g^{-1} in human lung samples (Rudolph et al, 2005b).

Establishing the described combination of matrix separation and selective enrichment allowed determination of Pd in human lung tissue for the first time. Excellent procedural limits of detection of 0.05 ng g^{-1} could be achieved. The LOD were was calculated including the whole sample preparation procedure (i.e. 2 step sample digestion, open vessel treatment followed by 2 step matrix separation procedure). Calculations were based on 3σ of $N = 4$ individually prepared, spiked blank solutions, which were also quantified by isotope dilution.

Table 2.1.3. Palladium concentration in human lung samples, the total combined uncertainty of the method is 17 % (coverage factor 2).

Sample Human lung	Measured value ($^{105}Pd/^{108}Pd$) / ng g^{-1} dry weight
1	1.4
2	1.2
3	0.26
4	0.93
5	1.2

As can be observed in Table 2.1.3, Pd concentration levels in the selected human lung samples were in the range of 0.3 and 1.4 ng g^{-1}. For all samples the values obtained for the two different isotope ratios (i.e. $^{105}Pd/^{108}Pd$ and $^{105}Pd/^{108}Pd$ agreed within their uncertainty, hence only the values obtained for $^{105}Pd/^{108}Pd$ are given in the text. The total combined uncertainty calculated according to EURACHEM/CITAC was 17 % applying a coverage factor of 2 (Eurachem 2000).

2.1.4 Conclusion

For the first time, palladium background concentrations in human lung samples were measured. As a matter of fact such investigations are imperative to assess the effective exposure and possible health risk for the human population. The developed analytical method is based on a 2-step matrix separation combined to a third pre-concentration step. As a key advantage the method is applicable to Pd trace analysis in human body fluids (Rudolph et al, 2005a) and diverse tissue samples enabling bio-availability studies in order to estimate the internal exposure to environmental palladium. So far it was only possible to assess Pt internal exposure. Since Pd shows a higher mobilization potential, human bio-monitoring studies are even more exigent.

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2.2 Determination of Palladium in Environmental Samples by ICP-MS after Preconcentration / Separation

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2.2.1 Problems of Pd determination in environmental samples

Palladium determination in environmental samples represents a new challenge, since this element, together with rhodium, is a major active component of recently developed car catalysts (Palacios et al. 2000). As a result of surface abrasion, these elements are released into the environment. The determination of this new pollutant at its environmental concentration (ng g^{-1}) requires the use of very sensitive analytical techniques such as Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Nevertheless, the accurate quantification of ultra-trace levels of Pd in autocatalyst-contaminated environmental samples such as airborne particulate matter, road dust or roadside soils by ICP-MS, is hampered by oxide, argide and doubly charged interferences resulting from the elements Cu, Cd, Pb, Y, Zr, Sr, etc. (Table 2.2.1). The latter may be originated from the catalyst matrix or from environmental pollution (Krachler et al. 1998, Gómez et al. 2000).

The resolution of a quadrupole (Q)-ICP-MS system is seldom sufficient to separate all palladium isotopes from their interferents. Mathematical models can be used for correcting these spectral interferences without extensive sample manipulation. However, the applicability of mathematical corrections depends on the magnitude of interference formation and is therefore affected by several factors, such as the Pd concentration in the sample, the concentration of interferent elements, the instrumental design and the instrumental operating conditions. For example, the Pd content in airborne particles from polluted areas is, in general, at the pg m^{-3} level, whilst the concentrations of Y, Zr, Sr, Cd are at the ng m^{-3} level and Cu and Pb at the μg m^{-3} level. This means that, after sample dissolution the interfering elements may reach a concentration which is of several orders of magnitude higher than the one of Pd. Gómez et al. (2000) calculated the average contribution (expressed as a percentage of 50 ng l^{-1} Pd content) of main interferent elements at their environmental concentrations in aqueous and airborne samples at different plasma RF power. The tremendous contribution of YO^+ (350-2000 %) or $ArCu^+$ (30-150 %) interferences on the

Table 2.2.1. Main potential interferences on Pd determination by ICP-MS.

Analyte		Interferent		Resolution required (m/Δm)[b]
Isotope	Abundance	Species	Abundance[a]	
^{104}Pd	11.14	$^{40}Ar^{64}Zn^+$	48.41	8500
		$^{88}Sr^{16}O^+$	82.36	33500
		$^{208}Pb^{2+}$	52.38	1200
		$^{104}Ru^+$	18.70	54700
^{105}Pd	22.33	$^{40}Ar^{65}Cu^+$	30.71	7300
		$^{89}Y^{16}O^+$	99.76	27600
		$^{88}Sr^{16}O^1H^+$	82.36	33500
^{106}Pd	27.33	$^{40}Ar^{66}Zn+$	27.79	7200
		$^{90}Zr^{16}O^+$	51.30	26500
		$^{106}Cd^+$	1.25	27900
		$^{89}Y^{16}O^1H^+$	99.76	27600
^{108}Pd	26.46	$^{40}Ar^{68}Zn^+$	18.72	6500
		$^{92}Zr^{16}O^+$	17.07	540000
		$^{92}Mo^{16}O^+$	15.01	40000
		$^{108}Cd^+$	0.89	1080000
^{110}Pd	11.72	$^{40}Ar^{70}Ge^+$	20.44	6000
		$^{94}Mo^{16}O^+$	9.33	20000
		$^{94}Zr^{16}O^+$	17.30	26800
		$^{110}Cd^+$	12.49	52300

[a]Maximum abundance possible calculated as the product of the natural abundance of the two isotopes forming the molecular ion divided by 100. [b]Minimum resolution to separate the interferent and analyte masses.

^{105}Pd signal (the isotope normally used because it is the most abundant and at the same time least subject to interferences) make mathematical corrections non suitable (Gómez et al. 2000, 2001).

Alternatively, instruments with a high-resolution magnetic sector-field (HR-ICP-MS) could be applied. However, even the maximum resolution power of $(m/\Delta m)=10{,}000$ is not sufficient to separate the YO^+ interference from ^{105}Pd. Equally the Cd^+ interference can not be resolved from $^{106}Pd^+$ or $^{108}Pd^+$, among others (Krachler et al. 1998).

As a result, when mathematical corrections or HR-ICP-MS can not be employed, the most frequently used approaches to address the problem of interferences are matrix separation by both, ion exchange or tellurium coprecipitation with or without previous fire assay. These methods have been extensively developed for Pd determination in geological samples (Barefoot and Van Loon 1999, Al-Bazi and Chow 1984). However, the application of these procedures to determine ultra-trace levels of Pd in environmental samples is not widespread and can be error prone. Difficulties related to the Pd determination can include incomplete recovery after sample preparation, sample digestion or matrix separation, as well as the risk of contamination during sample manipulation. As an example, Pd, in contrast to other platinum group elements (PGEs), binds strongly to silicate residues, even in acidic solutions, thus environmental samples have to be completely digested.

ICP-MS determination of trace constituents in complex samples is also susceptible to non-spectroscopic multiplicative interferences, typically suppression of analyte sensitivity, thus not only standard additions are recommended, but also the use of internal standards or better isotope dilution (ID). Unfortunately, a necessary condition for accurate determination with ID-ICP-MS is the availability of two isotopes free of spectroscopic interferences. Therefore, a complete separation of Pd from interfering elements is necessary prior to ID determination. The effectiveness of ICP-MS with and without ID, in combination with different separation procedures, has been validated by the successful determination of Pd at $\mu g\ g^{-1}$ level in geological and many other related samples, but few work has been carried out at the $ng\ g^{-1}$ level in environmental samples.

PGE determination in environmental samples without careful consideration of potential interferences and separation procedures can produce useless results, as has aptly been demonstrated by interlaboratory studies (Schramel et al. 2000). Methods that minimise sample manipulation, the number of reagents, their volumes, and which include adequate scope for the identification of interferences should be considered most appropriate

Table 2.2.2. Preconcentration /matrix separation methods for palladium determination in environmental samples by ICP-MS

Sample type	Sample digestion/pretreatment	Separation method/ Determination	Detection limit	Concentration range	Reference
Road soils	HF-$HClO_4$	NiS fire assay/ICPMS	0,20 ng g^{-1}	0.3-50 ng g^{-1}	Jarvis et al. (2001)
Fluvial sediments	Fusion	NiS fire assay/Te coprecipitation/ICPMS	0.35 ng g^{-1}	0.08-13 ng g^{-1}	de Vos et al. (2002)
Pine needles, airborne	Fusion	Pb fire assay/ICPMS	3 ng g^{-1}	1-45 ng g^{-1}	Dongarra et al. (2003)
Tunnel dust	Fusion	NiS-fire assay	----	6-90 ng g^{-1}	Zischka et al. (2000)
Ashed plant tissues	HF-*aqua regia*	Te coprecipitation/ETV-ICPMS	1 ng g^{-1}	no detect.-1350 ng g^{-1}	Dunn et al. (1989)
Ashed vegetation	Ashing 870ºC HF-aqua regia	Te coprecipitation/ID-ICPMS Pb fire assay/ ICPMS	1 ng g^{-1}	38-1620 ng g^{-1}	Hall et al. (1990)
Urban soils	*Aqua regia*-HF	Te coprecipitation/ICPMS	0.09 ng g^{-1}	1.1-101 ng L^{-1}	Morton et al. (2001)
Road dust, airborne	*Aqua regia*-HF/HCl	Te coprecipitation/ID-ICPMS	air: 0.6 pg m^{-3} dust: 1 ng g^{-1}	airborne: 5-32 pg m^{-3} road dust: 4-75 ng g^{-1}	Gómez et al. (2003)
Airborne, road dust, sewage sludge	Wet chemical digestion	Te coprecipitation/ ICPMS/HR-ICPMS NiS fire assay/ICPMS	0.4 ng g^{-1}	airborne: <28 ng g^{-1} road dust: <35 ng g^{-1} sludge: 300-450 ng g^{-1}	Shäfer et al. (1999)
Fresh water	10 % (v/v) HCl	Activated charcoal/ ICPMS/ETV-ICPMS	0.8/0.3 ng L^{-1}	< 5 ng L^{-1}	Hall and Pelchat (1993)
Airborne	*Aqua regia*/HCl	Modified silicagel (C18), ion pair / ICPMS	90 ng L^{-1}	no detect.-280 pg m^{-3}	Vlasánkova et al. (1999)

Table 2.2.2. (cont.) Preconcentration /matrix separation methods for palladium determination in environmental samples by ICP-MS

Environmental	HF-HBr	Anion exchange (TEVA)/ICPMS	0.3 ng g^{-1}	---	Makishima et al. (2001)
Marine water and sediments	KCN	Anion exchange/GFAAS	0.11 pmol kg^{-1}	water: 19-70 ng g^{-1} sediment: 2-46 ng g^{-1}	Lee (1983)
Environmental	---	Cation exchanger (AG 50W-X4)/DCPAES	3 µg L^{-1}	---	Strelow and Victor (1991)
Soils, grasses	*Aqua regia*-HF/HCl	Cation exchange (Dowex AG50W-X8)/ USN-ICPMS	10^{-3} pg g^{-1}	18-73 ng g^{-1}	Ely et al. (2001)
Road dust, roadside soil	*Aqua regia*/HF/ HNO_3/HCl	Cation exchange (Dowex AG50W-X8)/ ICPMS	13 ng L^{-1}	1.4-440 ng g^{-1}	Whiteley et al. (2003)
Environmental	---	C18 / N,N-diethyl-N´-benzoylthio-urea /GFAAS	13 ng L^{-1}	---	Shuster et al. (1996)
Biological materials	---	XAD-4 /bis(carboxylmethyl) dithio-carbamate/GFAAS	30 ng L^{-1}	---	Lee et al. (1993)
Car exhaust fumes, dust	*Aqua regia*-HF/HCl	Modified capillary (cation exchanger)/ MCM/DIN-ICPMS	MCM: 9 ng L^{-1} DIN: 6 ng L^{-1}	exhaust: 2.5-14 µg L^{-1} dust: 39-191 ng g^{-1}	García et al. (2001)
Urban water	2 % (v/v) HCl	Alumina microcolumn/ ICPMS	1 ng L^{-1}	10-45 ng L^{-1}	Moldovan et al. (2003)
Road dust, biological fluids	*Aqua regia*-HF	Sorption of diethylthiourea complex on PTFE knotted reactor/ USN-ICP-TOF-MS	0.36 ng L^{-1}	BCR-723	Benkhedda et al. (2003)
Road dust	*Aqua regia*-HF	Ion exchange (IonPac CS5A) /HPIC-ICP-SFMS Anion exchange (AG1-X8)/IDMS	HPIC: 13 pg IE: 70 pg	BCR-723	Hann et al. (2001)

2.2.2 Fire assay preconcentration of Pd

Fire assay techniques owe the majority of their development to the processing of geological samples (Oguri et al. 1999, Gros et al. 2002). Using relatively large sample sizes (4-100 g) and oftenly together with subsequent Te-coprecipitation, this technique has become well established for preconcentration. Lead and nickel sulphide are currently the most common collectors. The general procedure, using NiS as collector, consists in mixing the sample with a fluxing agent ($Na_2B_4O_7$, Na_2CO_3, SiO_2), Ni and S, then melting the blend in a fireproof crucible at temperatures up to 1100ºC. During fusion the Ni reacts with S to NiS, which after fusion, while cooling, aggregates to a button settling at the bottom of the crucible. During this process Pd is enriched in the NiS-button and simultaneously separated from most of the matrix elements. The separated NiS-button is then cut to small pieces and dissolved with HCl, while Pd and other insoluble noble metal sulphides remain in the residue. Palladium sulphide is filtered off, dissolved with H_2O_2/HCl or dil. HNO_3 and the resulting solution is analysed.

Both Pb and NiS fire assay techniques have been successfully applied to environmental samples, including road dusts (Zischka and Wegscheider 2000, Jarvis et al. 2001, Shäfer et al. 1999), pine needles (Dongarra et al. 2003) fluvial sediments (de Vos et al. 2002) and sewage sludge (Shäfer et al. 1999). Detailed information is shown in Table 2.2.2. Pd recoveries are around 90% (Zischka and Wegscheider 2000). Fire assay procedures can overcome issues of sample heterogeneity and reduce levels of matrix components to mitigate problems of interference formation. However, a significant drawback is that the selection of type and amount of flux agents and the appropriate furnace conditions is subjective, thus the quality of the results are to a large extent dependent on the operators experience. The large quantities of reagents used (for example more than 10 g of Ni in most NiS assay procedures) can elevate the signal in blank measurements to low ng g^{-1} levels (Ely et al. 2001). This limitation effectively precludes the reliable determination of Pd in environmental samples containing ultra-trace level of the element.

2.2.3 Coprecipitation with Te

Pd separation from matrix elements prior to its determination by ICP-MS has been achieved by coprecipitation with tellurium (Te) as carrier. General procedures consist in the reduction of the Te (IV) added to the sample to Te^0 by stannous chloride, which induces the Pd precipitation. Pd in an acid medium is equally reduced by stannous chloride, this step probably also involves the formation of a complex containing the noble metal in the neutral state $(Pd^{o}Sn_4Cl_4)^{4+}$. This complex normally breaks down upon boiling (Amosé 1998). After cooling, the black precipitate is filtered and dissolved with HNO_3.

Te-coprecipitation has been applied as a sole procedure, or following preconcentration by NiS fire-assay, for geological samples and also for fluvial sediments (de Vos et al. 2002). However, for the analysis of environmental materials where very low levels of Pd can be expected, Te-coprecipitation is more often employed as a sole precipitation technique. This is the case for the analysis of ashed vegetation (Dunn et al. 1989, Hall et al. 1990), airborne samples (Schäfer et al. 1999, Gómez et al, 2003), road dust (Gómez et al, 2003) and urban soils (Morton et al. 2001). Detailed information is shown in Table 2.2.2.

The effectiveness of the technique in the removal of interference forming matrix elements in environmental samples has been discussed. Hall et al. (1990) found that during the analysis of vegetation samples by Te coprecipitation, after ashing of 1-2 g of sample and further decomposition with *aqua-regia*-HF, up to 75% of Cu was also recovered. Gómez et al. (2003) showed that, although most of Cu and Y were removed (>95%) from the Te precipitate in the analysis of airborne and road dust samples (after digestion of 0.1-0.2 g sample with *aqua-regia*-HF), the remaining fraction in the precipitate produced a signal contribution to ^{105}Pd of about 1-10% from YO^+ and 1-15% from $ArCu^+$. This fact made it advisable to correct the contribution of these interferences mathematically. Recoveries within the range of 70-80 % and detection limits of 0.6 pg m^{-3} for Pd in airborne particulate matter and 1.0 ng g^{-1} for road dust were obtained. These authors compared the results obtained by external calibration (EC) and by ID after Te-coprecipitation. Both results agreed with the certified value for the road dust CRM BCR-723. However, in the case of ID, the standard deviation was lower than for EC, indicating a more precise methodology.

2.2.4 Sorption and ion exchange

Comprehensives reviews presented by Al-Bazi and Chow (1984), covering the period from 1950-83 and Barefoot and Van Loon (1999) for 1990-98 discussed solvent/sorbent extraction and ion exchange methods for PGE determination in a variety of samples, most of them from geological origin. Considering sorption processes, Pd adsorption (as chlorocomplex) onto activated charcoal has been used for fresh water samples from canadian mining areas (Hall and Pelchat 1993). Addition of concentrated HCl up to 1% (v/v) to freshly collected and filtered water samples prior adsorption was necessary to maintain Pd in solution at its natural concentration level in water (below 50 ng L^{-1}). Even then, stability after sampling beyond 20 days was questionable. *Aqua regia* was used to redissolve the adsorbed Pd, followed by ashing of the charcoal. In spite of previous removal of Y, Sr and Zr, originally present in the charcoal, interference corrections for YO^+ and $SrOH^+$ on ^{105}Pd and for ZrO^+ on ^{106}Pd were necessary. By this method Pd dispersion patterns in water from mineralised sites were identified.

Pd from airborne particulate has been separated and preconcentrated as ion pair of its chlorocomplex with the cationic surfactant N(1-carbaethoxypentadecyl)-trimethylammonium bromide (Septonex) on cartridges of modified silicagel (C18) (Separon^{TM} SGX). After Pd elution with ethanol, the eluate was evaporated in the presence of HCl (Vlasánkova et al. 1999). Preconcentration of two orders of magnitude, a detection limit of 90 ng L^{-1} and quantitative recoveries were obtained.

Ion exchange methods require the Pd to be present in appropriate chemical form, usually as anionic chloro or bromocomplex. Using anion exchanger columns/resins, the Pd is retained on the column and ideally separated from the concomitant interferent elements. When cation exchanger columns/resins are used, the Pd passes through the column while the interferent elements are retained. Final determination is, in most cases, carried out by ICP-MS, but GFAAS and DCP-AES can also be used at low concentration levels. A method using the TEVA resin (prepared by adsorbing Aliquat 336 on Amberlite XAD-7), which behaves as a strongly basic anionic resin, has been developed by Makisshima et al. (2001) for determination of Pd and other PGE (Ru, Os, Ir, Pt) in environmental samples. This method involves conversion of these elements into their bromo complexes by heating them with a HF-HBr mixture (these complexes present higher affinity for the resin that the corresponding chlorocomplexes), followed by elution from the resin by successive addition of HCl, HBr and HI. Recoveries for all the elements, including Pd, were higher than 90%, but the method is time consuming. Lee (1983), using anion exchange resins, determined Pd from marine water and sediments after a series of separation and concentration steps. Pd was isolated as cyanide complex from 2 L of seawater onto a small volume of anion exchange resin, eluted with hot 14 M HNO_3, evaporated to 1 ml and again retained onto a single anion exchange resin, which was finally inserted into GFAAS for analysis. The detection limit was 0.11 pmol kg^{-1}.

The strong cation exchange resin Dowex AG 50 W-X8 has been used for Pd analysis at ultra-trace level in soils and grasses from road sides (Ely et al. 2001). Detection limits for PGEs in the fg g^{-1} level were achieved, which allowed the application of this method to the determination of background levels for Pd, and consequently to evaluate the additional contamination of roadside media. Whiteley and Murray (2003) used the same approach for Pd determination in similar samples. Quantitative separation was obtained for Cu, Sr, Y, Hf and Pb, the maximum recorded levels of interferent (< 1g L^{-1}) did not induce any measurable signal on the Pd masses of interest. Pd recoveries ranged between 97-99 %. Strelow and Victor (1991) studied the ability of the cation-exchanger resins AG 50W-X8, AG 50W-X4, Dowex 50W-X8 and AG MP-50 to separate palladium from Cu and base metals which do not form stable chloride complexes, such as Ni, Fe (III), Zn, Mg, Ca, Al, Mn. AG 50W-X4 resin gave best results with detection limit of 3 μg l^{-1} by DCP-AES.

Schuster and Schwarzer (1996) proposed an on-line Pd preconcentration method with a microcolumn, loaded with the selective complexing agent N,N-diethyl-N´-benzoylthiourea, from where the Pd complex was eluted with 60 μl^{-1} ethanol achieving a detection limit of 13 ng L^{-1} for GFAAS determination. Lee and Tölg (1993) proposed an on-line sorbent extraction method for Pd preconcentration as its bis(carboxylmethyl)dithiocarbamate chelate on a microcolumn packed with XAD-4, further elution with 5 M NH_4OH gave a detection limit of 30 ng L^{-1} using GFAAS. In Table 2.2.2 these methods are summarised.

Although anion exchange procedures were most widely used for geological samples, for environmental samples, which contain Pd at ultra trace level, those based on cation exchange offer, in general, a number of advantages. As Pd forms an anionic chlorocomplex in dilute HCl media, it is not retained on cation exchange resins; thus the amount and concentration of acids employed are lower compared to anion exchange methods. Methods based on cation exchange are less costly and less time consuming, and therefore more suitable for routine analysis. Furthermore, problems of quantitative recovery of Pd at low concentration from anion exchange resins, mentioned by some authors (Al-Bazi and Chow 1984), are avoided. However, to avoid Pd chlorocomplex destabilisation and formation of aquocomplexes, which carry a lower charge than the former ones (even positive charges are possible), disolutions should be done immediately prior to loading onto the column and analysis should be completed within 3 days (Ely et al. 1999).

2.2.5 On-line methods for Pd preconcentration/matrix separation - ICP-MS determination

Off-line separation/preconcentration – determination methods present important drawbacks, such as time-consumption and important sample manipulation, thus increasing the risk of sample contamination and loss of Pd. On-line methods avoid most of these drawbacks. As in the case of off-line separation/preconcentration, some of them are based on the retention of Pd, others on the retention of the interferents. Cation exchangers, anion exchangers and other materials have been used for this purpose. A novel approach for on-line removal of interferences within modified capillaries coupled to micro-flow nebulizer-ICP-MS has been developed by García et al. (2001). A strong cation exchanger [2-(4-chlorosulfophenyl) ethyltrichlorosilane)] was covalently bound to the silica surface inside a capillary, which in turn was coupled to a microconcentric nebulizer (MCM) or to a direct injection nebulizer (DIN). The modified surface of the capillary was able to retain copper and yttrium from aqueous samples at pH 7.5 during the sample introduction step (the system allowed five successive sample injections), while Pd broke through and could be determined in the absence of the main interferent elements. The capillaries are easy to prepare and could be regenerated with several injections of 10^{-2} M HCl. Detection limits obtained, 8.8 and 5.8 ng L^{-1} for MCM and DIN, respectively were low enough for their application to road dust and car exhaust fumes.

A preconcentration method for PGEs, based on the sorption of their complexes formed on-line with diethylthiourea on the inner walls of a PTFE knotted reactor, has been proposed by Benkhedda et al (2003). Quantitative elution of PGEs was achieved by injecting 500 µL methanol acidified with 1% HNO_3. A complete separation from the matrix enabled interference free determination with a detection limit (reported for Pd by ultrasonic nebulisation-ICP-time of flight-MS) of 0.36 ng L^{-1}, which allows its application to biological fluids of healthy subjects and road dust. Moldovan et al. (2003) proposed a flow injection (FI) method incorporating an activated alumina microcolumn for effective on-line preconcentration of Pd in water. Filtered and stabilised in 2% (v/v) HCl, water samples were passed through the microcolumn at 3 mL min^{-1} for specified time periods to achieve retention of Pd and rejection of the sample matrix. Injection of 300 µL of 0.3 M KCN served to elute Pd from the microcolumn that was introduced on-line into the ICP-MS for determination. A sampling time of 10 min (30 mL) provided a limit of detection of 1 ng L^{-1}. This approach allows the on-line alleviation of primary ^{105}Pd interferences with Pd enrichment factors of about 100 and permitted Pd determination in urban water samples at the low ng L^{-1} level.

Two analytical strategies for Pd determination in geological and environmental matrices were evaluated by Hann et al. (2001), on-line high performance ion chromatography (HPIC)-HR-ICP-MS and off-line anion exchange with quantification by IDMS. In the on-line mode the system was equipped with a mixed bed ion exchange column (IonPac CS5A) using 2,6-pyridinedicarboxylic acid as complexing agent, providing a heterogeneous system which allowed both, cation and anion exchange. The off-line method was carried out using the anion exchanger AG1-X8 resin. The basic difference between the two methods is that the well established off-line method has to be blank-corrected for procedural blank levels, whereas for the on-line method it was found that blank correction can be performed by peak integration after baseline subtraction, being the latter significantly faster.

2.2.6 Conclusions

The development of preconcentration/matrix separation methods, which allow an accurate and precise determination of Pd in samples with very low analyte content, such as airborne particulate matter and water (that represent a potential risk for humans and the ecosystem), further able to distinguish contaminated from background levels, is of paramount importance. The important development of analytical methods in the last ten years highlights that, until methods are sufficiently developed and adopted as standards, the quality of environmental PGE concentrations will remain controversial.

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2.3 Sources of Error and their Elimination for Spectrometric Determination of Palladium in Environmental Samples

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2.3.1 Introduction

Despite recent advances in instrumental techniques the determination of palladium in environmental samples, such as urban aerosols, road and tunnel dust, is still a difficult task. Among various analytical techniques appropriate for the determination of low concentrations of palladium inductively coupled plasma mass spectrometry (ICP-MS) and graphite furnace atomic absorption spectrometry (GFAAS) are most often used. However, the determination of palladium in environmental samples by spectrometric techniques is strongly hampered by numerous spectral and non-spectral interferences arising from a complicated sample matrix. In order to obtain reliable results it is crucial that all sources of interferences are identified and initial sample pre-treatment steps, such as sample digestion, storage, pre-concentration of analyte, and separation of matrix, are carefully controlled in respect of palladium chemistry and introduction of potential interferences.

This paper deals with critical points in palladium determination by atomic spectrometric techniques, which may obscure receiving accurate results. The advantages and limitations of selected digestion, separation and pre-concentration procedures as well as analytical problems which may occur during preparation and storage of samples for palladium analysis are specially emphasised. The procedures for determination of palladium in environmental samples by GFAAS and ICP-MS developed by authors are also presented.

2.3.2 Limitations of spectrometric techniques (GFAAS, ICP-MS)

The drawbacks of using of GFAAS for the determination of palladium are: detection limit, insufficient for environmental materials, and occurrence of spectral interferences, which are usually caused by incompletely compensated background signal of matrix origin. The presence of Fe, Pb, Ni, Zn, and Co at µg/g concentration causes the change in palladium absorbance signal at λ=247.6 nm in the range from +40% to –50%, depending on the metal concentration (Leśniewska 2004). The increase of pyrolysis temperature or the measurement of palladium signal at alternative lines can partially compensate this effect. Nevertheless, pre-concentration and matrix separation procedures are essential prerequisites for determination of palladium in environmental samples by GFAAS.

The determination of palladium by ICP-MS is disturbed by spectral interferences from isobaric ions formed in plasma by geologically abundant elements such as Cu, Zn, Sr, Y, Cd, Mo, Zr with non-metals. Considering the relatively high Zr, Cd and Y concentrations in environmental samples and the high ability of Zr and Y to form interfering molecules in the plasma, the most serious interferences on ^{105}Pd, ^{106}Pd and ^{108}Pd isotopes are caused by ^{89}Y^{16}O^{+}, ^{106}Cd^{+}, ^{90}Zr^{16}O^{+}, ^{108}Cd^{+}, ^{92}Zr^{16}O^{+} ions (Bencs et al. 2003). The instruments with a high-resolution (HR) magnetic sector-field (SF) allow often for separation many polyatomic interferences, but the mass resolution required for the elimination of interferences from ^{90}Zr^{16}O^{+}, ^{89}Y^{16}O^{+} and ^{88}Sr^{17}O^{+} on ^{105}Pd and ^{106}Pd is, at present, not commercially available.

The methods of overcoming these interferences were discussed in details by Bencs et al. (2003). Basically, in selection of the isotope for measuring, the composition of the sample should be considered. When simple samples are analysed, e.g. polar and alpine snow (Barbante et al. 1999), the most abundant ^{106}Pd isotope is preferred. In analysis of more complex samples, such as soil or road dust, the use of the ^{105}Pd isotope, which is less abundant but also less hampered by the high Cd and Zr concentration, is recommended (Petrucci et al. 2000, Rauch et al. 2000). The careful optimisation of instrumental conditions partially reduces the interferences to the analyte signal. Additional correction procedures as alternative sample introduction systems (ultrasonic nebulization, membrane desolvation units), use of collision cells and dynamic reaction cells, and/or mathematical correction have been also proposed.

Mathematical correction method, based on the evaluation of the actual influence of interferent on analytical signal, may provide accurate results for the determination of palladium in relatively simple matrices, such as urine (Krachler et al. 1998) or polar snow (Barbante et al. 1999). In the case of road dust and sediment samples, very high concentration of Zr and Cd preclude the application of any mathematical correction method for determination of ^{106}Pd and ^{108}Pd. In addition, the enormous interference from ^{89}Y^{16}O+ on ^{105}Pd makes impossible its accurate determination (Djingova et al. 2003).

Application of an ultrasonic nebuliser (USN) coupled to the ICP-SFMS instrument, instead of conventional pneumatic nebuliser, enhances sensitivity and the detection power of palladium in model solution by one order of magnitude, but is not sufficient for the removal of isobaric interferences during palladium determination in environmental samples (Rauch et al. 2000). Combination of the mathematical correction method and USN-ICP-SFMS allow obtaining only indicative values for palladium content in road dust (Petrucci et al. 2000). The membrane desolvation systems used for elimination of spectral interferences formed by oxide and chloride molecular ions are also inefficient for palladium determination (Kanitsar et al. 2003). Coupling of membrane desolvation system with ultrasonic nebuliser and ICP-SFMS instrument and finally with mathematical correction of interferences caused by $^{88}Sr^{16}O^{1}H^{+}$ ions finally made possible accurate determination of palladium in environmental samples (Köllensperger et al. 2000). The presented strategies need advanced technical devices not often available in routine laboratories, therefore for accurate determination of palladium by ICP-MS the chemical separation of analyte from interfering elements is still a method of choice.

2.3.3 Problems connected with chemistry of palladium in solution

Many analytical problems occurring during palladium analysis arise from the complex nature of its solution chemistry. Palladium occurs in numerous oxidation states (I, II, IV) and forms many species in a given oxidation state. As it belongs according to Pearson theory to the "soft" acids it easily forms halides, hydrides, cyanides, and other complexes with ligands containing sulfur and nitrogen donor atoms. The palladium coordination compounds in aqueous solutions have different stability and kinetic properties. Palladium is usually present in solutions as $Pd(H_2O)_4^{2+}$. The formation of $PdOH^+$ and $Pd(OH)_2$ starts at pH above 1 and insoluble $Pd(OH)_2$ precipitates from diluted nitric acid solutions. The evidence of formation of $PdNO_3^+$, $Pd(NO_3)_2$ and $Pd(OH)NO_3$ in nitric acid has been also shown (Camacho Frias et al. 1995). Above pH 2 polynuclear forms have been identified.

The palladium chloride complexes are more stable than nitrate complexes. Different pH and chloride concentration leads to a different distribution of chloro complexes of palladium in aqueous solutions. At pH 1.0 the complex $PdCl_4^{2-}$ is predominant (90-100%), at pH 2.0 the fraction of the complex $Pd(H_2O)Cl_3^-$ reaches a maximum value (30-40%), while at pH 2.3 $Pd(H_2O)_2Cl_2$ becomes more important (>80%) (Iglesias et al. 1999).

However other studies showed that at pH 3 palladium is present in the form of $PdCl_3^-$ in a wide range of chloride concentration. At higher temperatures (55°C) the change of stability constants of chloro complexes of palladium occurs what results in predominance of $PdCl_4^{2-}$ (Pirogov and Havel 1997). Hence, in the digested sample solution, depending on the pH and chloride concentration, different species of palladium can be present.

Compounds of palladium have also the tendency for sorption and reduction of their oxidation state. The interactions between the solution and the surface of laboratory vessels may cause losses of analyte during storage and pre-treatment steps. The properties of the container, such as its chemical composition and surface roughness may influence the process of adsorption. Those effects were only rarely mentioned, in spite of the fact that they may seriously influence the analytical results. The 10% decrease of absorbance was observed when solutions of palladium and other platinum group elements (PGEs) prepared in 1% HNO_3 were left for a few hours in polystyrene autosampler cups. This problem did not occur with solutions prepared in 1% HCl or stored in glassy cups (Byrne et al. 1997). Although containers made of polyethylene and PTFE are most often used in trace analysis the use of quartz vessels provides better stability of dilute palladium solutions and higher values of absorbance measured by GFAAS technique. The studies performed on the stability of Pd(II) standard solutions stored in different containers have shown that the highest losses of analyte were observed in polyethylene and polyethylene-polypropylene vessels (Godlewska-Żyłkiewicz 2002). It should be stressed that for the stabilization of samples containing palladium addition of HCl is recommended (Godlewska-Żyłkiewicz et al. 2000). Large non-polar complexes of palladium with organic ligands, e.g. with dithiocarbamates or thiourea derivatives (Benkhedda et al. 2003) may be easily adsorbed on hydrophobic materials of system manifolds as surface of tubes or columns. The memory effects and/or analyte losses may also occur in such systems.

Losses of palladium were also observed when solution containing known amounts of PGEs was evaporated directly in glassy carbon crucible indicating some physical or chemical reactions occurring between the analyte and the crucible material (Enzweiler et al. 1995). Other investigations had showed that reduction of palladium ions to metallic palladium on the surface of graphite or glassy carbon occurs from diluted nitric acid solutions (Godlewska-Żyłkiewicz and Zaleska 2002, Komarek et al. 1999). The chloro complexes of palladium formed in hydrochloric acid prevent the reduction of palladium on the carbon surface. Application of zirconium crucibles for sample decomposition (alkaline fusion) could lead to low recoveries of palladium (75%) due to its adsorption on hydrated zirconium dioxide (Enzweiler and Potts 1995). On the other hand zirconium originating from ball mills, borosilicate glass digestion vessels or leached from crucibles significantly interferes in the determination of palladium by ICP-MS.

Although palladium is an element with the lowest abundance in the earth's crust the use of contaminated materials or tools during any step of analysis may introduce significant errors in its determination. Sample preparation steps should be carried out under clean room conditions. The ultrapure reagents and materials (sub-boiled acids, clean resins), appropriate vessels for sample storage and preparation (tubes, crucibles) and tedious cleaning procedures are necessary to avoid contamination of the samples and to reduce a procedural blank.

2.3.4 Sample digestion procedures

When critically assessing digestion technique a number of factors must be considered, as: complete dissolution of analyte, potential loss of analyte during digestion, and final form of analyte in the mineralised solution, which must be suitable for the pre-treatment procedure and detection technique of choice.

Palladium in geological samples may occur in discrete potentially soluble mineral grains, or may be embedded within refractory chromites and/or silicate minerals. Palladium in environmental samples is present mainly in elementary, more accessible, form (Müller and Heumann 2000) since it originates from catalytic converters of motor cars. Different sample decomposition methods such as digestion with mineral acids in open vessels (Benkhedda et al. 2003, Kanitsar et al. 2003, Kovacheva and Djingova 2002, Limbeck et al. 2003), high-pressure ashers (Müller and Heumann 2000), microwave digestions (Boch et al. 2002, Köllensperger et al. 2000) and fusion with sodium peroxide (Enzweiler and Potts 1995) prior to the determination of palladium have been reported. Microwave digestion allows the more rapid dissolution of materials and reduces the amount of reagents required compared with the open acid method. The efficiency of various acid leaching procedures has been studied extensively, but by far the most popular reagent is *aqua regia* (Kovacheva and Djingova 2002, Müller and Heumann 2000). The use of acids with high boiling point e.g. $HClO_4$, accelerates the dissolution of the resistant products containing palladium and oxidation of organic material (Limbeck et al. 2003, Kanitsar et al. 2003). For complete sample digestion the use of *aqua regia* in combination with HF is necessary.

Contradictory reports can be found in the literature on the necessity of using of HF prior to the determination of palladium. It has been reported that palladium strongly binds to silicate matrix of dust or to ceramic particles of the catalyst released to environment (Benkhedda et al. 2003, Kanitsar et al. 2003), so additional HF attack must be employed in the digestion procedure (Köllensperger et al. 2000, Kanitsar et al. 2003, Boch et al. 2002). However, other investigations showed that the application of HF did not cause higher mobilization of palladium from street dust samples (Kovacheva and Djingova 2002, Müller and Heumann 2000). We confirmed that treatment of road dust samples with *aqua regia* let obtain the total recovery of Pd from certified reference material BCR-723. The content of Pd in BCR-723 determined by ICP-MS (7.2 ± 1.0 ng/g) (Leśniewska 2004) agreed well with the certified value (6.0 ± 1.8 ng/g) (Zischka et al. 2002).

The application of HF for digestion has some disadvantages. The presence of HF in digested sample solution may cause the corrosion of sample introduction system in ICP-MS apparatus, or destroy the silica columns used for matrix separation (Boch et al. 2002). Acid attack with HF is usually followed by evaporation step to remove silica and fluoride, as the volatile silicon tetrafluoride, SiF_4. Overheating of the sample for an extended period can result in low yields either through losses of volatile species or enhancement of interferences. In the absence of solvents irreversible adsorption of palladium on the surface of reaction vessel could occur, and the dry residue could be only partially dissolved with diluted HCl. To avoid the evaporation of HF prior to the measurement step the addition of H_3BO_3, for masking of fluoride ions, was proposed. However, this reagent causes interferences during palladium determination by ICP-MS (Köllensperger et al. 2000), and positive results could only be obtained when additional matrix separation step was applied (Boch et al. 2002). The other potential difficulty is that more interfering Zr and other metals are released form soil samples after the total digestion.

It is worthwhile to stress that the chemical forms of the PGEs after digestion of real sample may not be identical to those found in standard solution. Pre-treatment procedure of samples dissolved in *aqua regia* must include elimination of nitrates from the solution, because stable nitrites of platinum and palladium behave differently to chloride complexes. In this case double evaporation with HCl to ensure conversion of palladium into the chloride form is recommended, especially if the latter ion-exchange separation is carried out. As in the presence of HF fluoride complexes of other metals (e.g. YF_4^-) might be formed, they can pass through the cation-exchange column together with the analyte.

2.3.5 Separation/pre-concentration procedures

Among various procedures used for the pre-concentration/separation of palladium (Godlewska-Żyłkiewicz 2004), solid phase extraction (SPE) based on different interactions between the analyte and the solid sorbent has found one of the most important positions.

Ion-exchange methods are based on the fact that palladium forms highly stable anionic chloro complexes, while other metals form weaker anionic or stable cationic species. Prior to any ion-exchange separation it is essential that the palladium is fully in a suitable chemical form. The interfering cations are exchanged and adsorbed on the cation-exchange resin, while the analyte is passed through the clean-up column. The efficiency of such separation depends on the kind of resin, acidity of the sample, presence of sufficient amount of chloride ions, size of the column and mesh of the resin, as well as occurrence of other complexing reagents in the sample solution.

The efficiency of matrix separation by cation exchangers was assessed using Dowex 50WX-2, Dowex HCR-S, Varion KS, Cellex-P and Dowex 50WX-8. The initial investigations have shown, that the latter has the best characteristic (Table 2.3.1). When the concentration of HCl is too low (below 0.05 mol/l), palladium cannot efficiently form complex anions and is adsorbed on the cation-exchange resin. Fig. 2.3.1 shows that small losses of palladium from 0.5 mol/l HCl may also occur on too large columns, and the use of resins of higher mesh (50-100) is preferable as cations are better retained on such resin. Columns that have been used many times before tend to retain more palladium that columns containing new resin.

Another potential difficulty of using cation-exchangers is passing through the column, together with $PdCl_4^{2-}$, metals which form oxide interferences on the most of palladium isotopes as Zr, Mo and Y. It was found that a significant amount of yttrium was not retained on the column from road dust (25%) and tunnel dust (49%), when samples were digested with

Table 2.3.1. Recovery of palladium (1 ng) from synthetic solutions by ICP-MS after elimination of interferences on Dowex 50WX-8 (2g, mesh 50-100) (n = 6)

Sample matrix (1 ng Pd)	Pd recovery [%]
0.5 mol/l HCl	94.2 ± 0.4
0.5 mol/l HCl + 0.7 mol/l HNO_3	88.4 ± 0.6
0.05 – 2.5 µg Hf, Zr, Y, Sr, Cu, Zn in 0.5 mol/l HCl	89.1 ± 1.7
0.5 – 25 µg Hf, Zr, Y, Sr, Cu, Zn in 0.5 mol/l HCl	89.5 ± 1.0

HF, indicating that neutral or negatively charged fluorocomplexes of yttrium have been formed. Therefore the use of such procedures in connection with isotope dilution (ID) ICP-MS is problematic with respect to elimination of interferences from metals forming polyatomic ions. The quantitative retention of yttrium (99.9%) on Dowex 50WX-8 was observed when samples were digested with *aqua regia*. The content of palladium in road dust BCR-723 determined by ICP-MS after matrix separation on Dowex 50WX-8 was 7.2 ± 1.0 ng/g (Leśniewska 2004), while the certified value is 6.0 ± 1.8 ng/g (Zischka et al. 2002).

The sorption ability of anion-exchange resins is quite different for various species. The higher oxidation states of PGEs are more strongly sorbed by anion resins, whereas lower oxidation states and less charged species are more weakly bound. Formation of hydroxycomplexes of a smaller charge leads to a decrease in the sorption efficiency on such resins. Another problem with strong anion exchangers is that commercially available resins do not selectively adsorb palladium chloro complexes. The elements that form anionic complexes during digestion procedure (Ti, V, Al, Fe, Ce, Pb, Zr, Cu, and Y) can be also enriched on such resins (Kovacheva and Djingova 2002). However the addition of masking agents should be avoided as they can change the chemical form of palladium. In many cases the recovery of noble metals from strong anion-exchange resins is not quantitative. There-

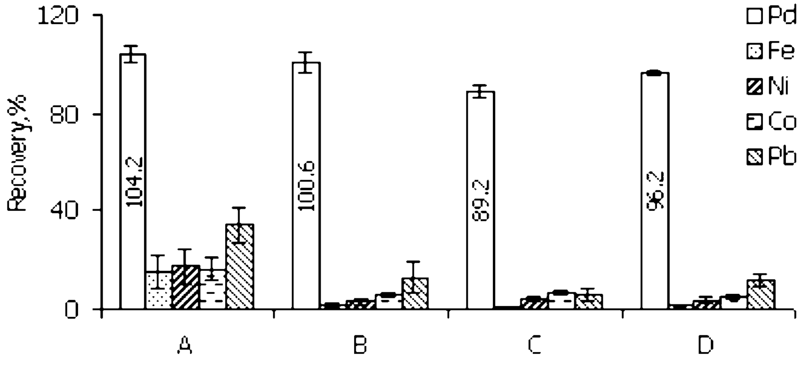

Fig. 2.3.1. Recovery of Pd (150 ng) and Fe (1 mg), Ni (0.5 mg), Co (0.5 mg), Pb (1 mg) determined by GFAAS from solution passed through cation-exchange resins: A – Dowex 50 WX-8, 20-50 mesh, 2g; B – Dowex 50WX-8, 50-100 mesh, 2g, C - Dowex 50 WX-8, 50-100 mesh, 4g; D – Varion KS, 4g

fore, the ID technique is especially advantageous because partial loss of analyte has no effect on the analytical results (Kanitsar et al. 2003). Since polyatomic interferences on some isotopes may preclude this approach for some sample types, the careful control of isotopic ratios must be performed. The total recovery of palladium has been achieved by digestion of the resin, by elution with large volumes of hot concentrated nitric acid or specific palladium complexing reagents. The main advantage of using weakly basic cellulose exchangers e.g. Cellex-T (containing Quarternary amine functional groups) is a quantitative recovery of palladium retained on the column with relatively small volume (2-5 ml) of diluted thiourea (TU) solution (Godlewska-Żyłkiewicz et al. 2000).

The main limitation in application of anion-exchangers in pre-concentration procedures comes from the fact that environmental samples contain high amounts of inorganic ions which overload the capacity of these sorbents. Therefore the combination of cation and anion-exchangers is proposed.

Because the total retention of palladium on Cellex-T was achieved from solutions of pH>4, to avoid hydrolysis and precipitation of other ions the sample clean-up procedure by means of Dowex 50WX-8 was performed for real samples. The quantitative elution of palladium was obtained for 0.1 mol/l TU in 2 mol/l HCl (Table 2.3.2). The described method was applied for determination of palladium by GFAAS in highly contaminated samples (Pd content > 100 ng/g). When using the evaluated procedure for determination of palladium by ICP-MS unidentified interference occurred, causing the palladium recovery from road dust and BCR-723 above 200%. The low content of yttrium and strontium determined in eluate indicated that these metals can not be a source of such interference. Probably the used eluent partially destroys the resin, and such „particles“ introduced into plasma of MS caused interference during palladium measurements. It is worth mentioning that the accurate results were obtained for Pt determination when the described above procedure was applied (Leśniewska 2004).

The pre-concentration based on the biosorption of analyte by micro-organisms is one of the variants of SPE technique. In this case binding of metal ions is attributed to various mechanisms such as ion-exchange, adsorption, complexation, and micro-precipitation depending on kind of used micro-organism and studied metal. The procedures developed for selective accumulation of palladium (together with platinum) on algae *Chlorella vulgaris* immobilized on silica gel (Godlewska-Żyłkiewicz 2003) and Cellex-T resin (Dziwulska et al. 2004) were applied for the determination of palladium in spiked waste water and grass samples by GFAAS.

Table 2.3.2. Recovery of palladium from road dust after matrix separation on Dowex 50WX-8 (2g, 200-400 mesh) and palladium pre-concentration on Cellex-T (0.2 g)

Sample	Eluent	Eluent volume [ml]	Determination technique	Pd recovery [%]
Road dust*	2 mol/l HCl	4	GFAAS	73.5 ± 4.9
Road dust*	0.25 mol/l TU +1 mol/l HCl	2 + 2 3 + 2 5	GFAAS	80.6 98.3 97.6
Road dust*	0.1 mol/l TU+ 2 mol/l HCl	4	GFAAS	102.9± 4.7
Road dust	0.1 mol/l TU + 1 mol/l HCl	4	ICP-MS	>200
BCR-723	0.1 mol/l TU + 1 mol/l HCl	4	ICP-MS	>200

*spiked with 40 ng of Pd

Using yeast *Saccharomyces cerevisiae* immobilized in calcium alginate results in accurate palladium determination in road dust samples and geological materials (Godlewska-Żyłkiewicz and Kozlowska 2005).

Although the procedures based on SPE concept are still the most popular, alternative methods of palladium separation have been also proposed. The main advantage of separation of palladium by reductive co-precipitation with mercury is that the used collector can be efficiently removed from the sample at 300°C. The procedure followed by total reflection X-ray fluorescence (Messerschmidt et al. 2000) was successfully applied for analysis of road and air dust (Zereini et al. 2004). Electrolytic reduction of palladium at controlled potential on the graphite or glassy carbon electrodes in a flow-through mode was followed by its electrochemical dissolution with the aid of appropriate stripping reagent. The proposed procedure was used for the determination of palladium in road dust samples by GFAAS (Godlewska-Żyłkiewicz and Zaleska 2002).

2.3.6 Conclusions

Accurate determination of trace amounts of palladium by spectrometric methods (GFAAS, ICP-MS) is practically impossible without chemical pre-concentration/separation procedures. The matrix composition and the elements introduced in the course of sample dissolution, also due to contamination, significantly influence the proper choice of the determination technique. Until now the new technical developments, in particular for ICP-MS, not always offer the best way of elimination of the interferences. The use of HF for sample digestion must be critically evaluated, as in some cases it may introduce serious errors. The variety of chemical forms of palladium in the final solution may also affect the results of spectrometric determination. Attention should be paid to the material of the laboratory ware to avoid losses due to adsorption and carryover of the analyte in subsequent analyses. The most reliable way for identification and elimination of errors is always the use of certified reference materials.

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2.4 Collision Cell ICP-MS as Tool for the Determination of Palladium

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2.4.1 Introduction

The introduction of catalytic converters has significantly reduced emissions of carbon monoxide, hydrocarbons, and nitrogen oxides produced by vehicles equipped with combustion engines that use fuels derived from fossil fuels. The vehicles range from passenger cars to heavy duty trucks. Palladium, platinum and rhodium (platinum group elements, PGE) are the main active components of these autocatalysts. Chemical deactivation, thermal and/or mechanical deterioration modify the surface structure of the catalytic converter, favouring the release of PGE into the environment (Moldovan et al., 2002). The number of vehicles fitted with palladium-containing catalytic converters is increasing, and consequently palladium content in environmental samples is gaining importance.

Palladium concentration in environmental samples is typically low and its determination requires the use of very sensitive analytical techniques. Inductively coupled plasma-mass spectrometry (ICP-MS) allows the rapid determination of palladium at trace and ultra-trace level, but it suffers from spectral interferences (Krachler et al., 1998). Spectral interferences are the combined factor of very low palladium concentration and a matrix with high content of interfering elements arising for the catalyst abrasion or atmospheric pollution. Table 2.4.1 shows the existing naturally occurring isotopes of palladium with their most common spectral interferences and the resolution required for their separation. ^{105}Pd is the palladium isotope generally used because it is one of the most abundant and, at the same time, it is the least subject to interference in ICP-MS.

Table 2.4.1. Naturally occurring isotopes of palladium, their spectral interferences and the required resolution for their separation

Mass	Abundance, %	Interferences (abundance, %)	Resolution ($\Delta m/m$)
^{104}Pd	11.14	^{40}Ar^{64}Zn (48.41)	8500
		^{88}Sr^{16}O (82.36)	33500
		^{208}Pb (52.38)	1200
		^{104}Ru (18.70)	54700
^{105}Pd	22.33	^{40}Ar^{65}Cu (30.71)	7300
		^{89}Y^{16}O (99.76)	27600
^{106}Pd	27.33	^{40}Ar^{66}Zn (27.79)	7200
		^{90}Sr^{16}O (51.34)	26500
		^{106}Cd (1.25)	27900
^{108}Pd	26.64	^{40}Ar^{68}Zn (18.72)	6500
		^{92}Sr^{16}O (17.07)	540000
		^{92}Mo^{16}O (15.01)	40000
		^{108}Cd (0.89)	1080000
^{110}Pd	11.72	^{40}Ar^{70}Ge (20.44)	6000
		^{94}Mo^{16}O (9.33)	20000
		^{94}Zr^{16}O (17.30)	26800
		^{110}Cd (12.49)	52300

The resolution of quadrupole ICP-MS is seldom sufficient to separate palladium from its interferences. Although mathematical models could usually correct for the spectral interferences in ICP-MS, depending on the type of samples they are not always enough for this purpose.

In order to overcome spectral interferences, different instrumental and chemical methods have been proposed. Instruments with a high resolution magnetic sector field (ICP-SFMS) could be applied. However, even working at the maximum resolution power ($\Delta m/m = 10000$) it is not sufficient to separate ^{89}Y^{16}O interference from ^{105}Pd (Rauch et al., 2000). Different introduction methods such as desolvation (Kanistar et al., 2003) and laser ablation (Motelica-Heino et al., 2001) have also been used to minimize interferences as no solvent is introduced into the ICP-MS. Among chemicals strategies we could mention matrix/analyte separation due to: anionic or cationc chromatography (Kanistar et al., 2003; Meisel et al., 2003), tellurium coprecipitation (Gómez et al., 2003), modified capillaries coupled to micro-flow nebulizers (García et al., 2001) and alumina microcolumns (Moldovan et al., 2003). Furthermore, isotope dilution ICP-MS coupled to matrix separation gave good results for Pd quantification (Müller and Heumann, 2000).

2.4.2 Collision/reaction cell ICP-MS

Recently, collision/reaction cells have given new possibilities to quadrupole mass analyzers used in ICP-MS. Such post-plasma methods that are applied to the interferences have the advantage that they do not interfere with instrument operating conditions or plasma chemistry.

With this approach, ions enter the interface in the normal manner, where they are extracted under vacuum into a collision/reaction cell (quadrupole, hexapole or octapole) that is positioned before the quadrupole analyzer. The cell, filled with one or more collision gases, typically operates in the radio frequency (rf) mode. The rf-only filed has the effect of focusing the ions, which then collide and react with molecules of the collision/reaction gas. Due to different ion-molecule collision and reaction mechanisms, polyatomic interfering ions will either be converted into less non-interfering species, or the analyte will be converted to another ion which is not interfered with. Fig. 2.4.1 shows the scheme of a typical collision/reaction cell ICP-MS instrument.

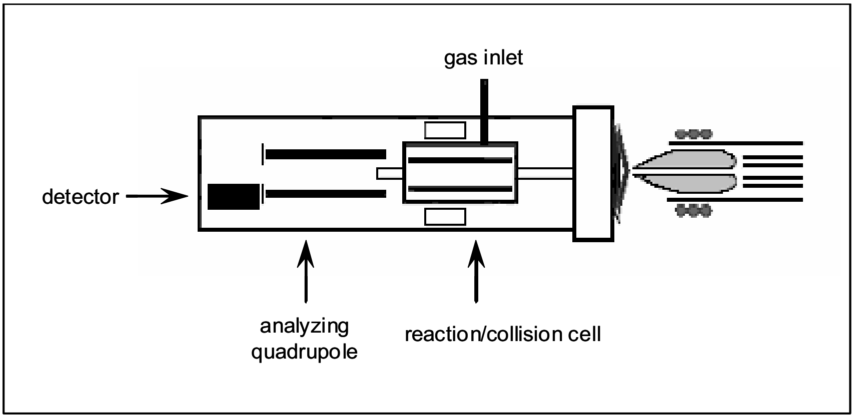

Fig. 2.4.1. Scheme of a collision/reaction cell ICP-MS instrument

Within the cell, complex secondary reactions and collisions take place, which generate many undesirable interfering species. Discrimination by kinetic energy or mass is used to reject the products of these unwanted interactions, which could potentially lead to additional spectral interferences (Tanner et al., 2002).

Originally collision/reaction cells were used in ICP-MS to stop the appearance of many argon based spectral interferences. However, recently such technology was also applied on the attenuation of interferences related with PGE analysis.

Simpson et al (2001) made use of a dynamic reaction cell (DRC) in combination with O_2 as reaction gas to promote oxidation of the elements that interfere with the noble metals to higher oxides, with a resulting separation of analyte from interfering species. An optimized cell gas flow of 2.3 mL min^{-1} effectively separated each analyte interference pair studied: $^{106}Pd/^{90}Zr^{16}O$, $^{107}Ag/^{91}Zr^{16}O$, $^{108}Pd/^{92}Zr^{16}O$, $^{194}Pt/^{178}Hf^{16}O$, $^{195}Pt/^{179}Hf^{16}O$, $^{197}Au/^{181}Ta^{16}O$. Kan and Tanner (2004) developed a method for the analysis of low concentrations of Pt in road dust by DRC-ICP-MS employing NH_3 (1.05 cm^{-3} min^{-1}) as reaction gas. In a similar way, Vanhaecke et al. (2004) proposed the use of NH_3 as a reaction gas (flow rate 0.2 Ar-equivalent mL min^{-1}) in a dynamic reaction cell to overcome $^{103}Rh^{+}/^{206}Pb^{2+}$ overlap without disturbing the determination of Pt and Pd. The capability of this approach was evaluated by analyzing Pb buttons obtained by fire assay of platiniferous ores.

The present chapter describes the use of NH_3 diluted in He as collision gas for the analysis of palladium by collision cell ICP-MS.

2.4.3 Experimental

Reagents

All chemicals were of analytical-reagent grade unless indicated otherwise. Calibration and working standard solution were prepared daily in low-density polyethylene (LDPE) containers by diluting stock standard solution of Pd, Y, In and Ce (1000 mg L^{-1}). Nitric, hydrochloric and hydrofluoric acids were of Ultrex quality (JT Baker). Pure water from a Milli-Q system was used throughout for preparing sample solutions.

Samples

Road dust was collected in the Somport Tunnel. This tunnel (connecting Spain to France, and opened in January 2003) will represent a clear increase on road traffic density, especially of heavy duty trucks, in the Aspe Valley (Atlantic Pyrenees). 0.1 g (< 63 µm fraction) were digested with 8 mL *aqua regia* and 1 mL HF in a microwave oven (Anton Paar, multiwave 3000) The digested samples were transferred to PTFE vessels and heated to dryness on a hot plate. 2 mL HCl were added and heated to dryness (repeated twice). Finally, the residue was made up to 25 mL with 2% HCl (v/v).

In order to estimate the accuracy of the proposed method, the certified reference material BCR 723 (road dust) was analyzed.

Instrumentation

A Thermo X7 Series ICP-MS (Thermo Electron Corp., Winsford, Cheshire, UK) was used. The instrument was operated in collision cell mode, using 1% NH_3 in He (Air Liquide, Mitry-Mory, France) as collision gas. This gas was used without further purification. In order to minimize contamination, Baked stainless-steel transfer lines and Swagelok fittings were used to connect the gas bottle to the instrument. The operating conditions of the instrument are listed in Table 2.4.2.

Table 2.4.2. Instrumental operating conditions

Parameters	Values
Forward power	1350 W
Plasma gas flow rate	15 L min^{-1}
Auxiliary gas flow rate	1 L min^{-1}
Nebulizer gas flow rate	0.75 L min^{-1}
Nebulizer	conical
Spray chamber	Peltier-cooled impact bead (1°C)
Cones	nickel
Working isotopes/ions	^{89}Y, $^{89}Y^{16}O$, ^{105}Pd, ^{115}In, ^{140}Ce, $^{140}Ce^{16}O$
Sweeps	100
Dwell time	10
Channels	3

Table 2.4.3. Collision cell parameters

Parameters	Values
Pole bias	- 1.5 V
Hexapole bias	- 3.5 V
Collision gas flow rate (1% NH_3 in He)	1 mL min^{-1}

2.4.4 Results

Optimization of the collision cell

The instrument was tunned daily by varying the instrumental parameters to get maximum signal intensity for ^{115}In and minimum level of oxides ($^{140}Ce^{16}O/^{140}Ce$ ratio) using a 1 µg L^{-1} tune solution.

In addition, ^{115}In signal and $^{140}Ce^{16}O/^{140}Ce$ ratio were monitored during all the experiments carried out. The bond strength of CeO (795 kJ mol^{-1}) and YO (719.6 kJ mol^{-1}) have similar magnitude, and therefore a parallel behaviour for both polyatomic species is expected.

Under collision cell mode analysis some parameters such as the hexapole bias voltage, the pole bias voltage and the collision gas flow rate have to be optimized. These parameters will determine the number of collisions occurring in the reaction cell. The reaction gas passes through the cell continuously and the optimum flow rates required are determined by measuring the lowest $^{89}Y^{16}O/^{89}Y$ and $^{140}Ce^{16}O/^{140}Ce$ ratios and maximum ^{115}In signal against changes in the reaction gas flow rate. This step is necessary to determine the point at which complete interference removal has occurred and signal to noise ratios of the analyte are sufficient for the measurement. Table 2.4.3 presents the optimized collision cell parameters used within this work.

Collision cell analysis

The analysis of solution of yttrium at different concentrations (prepared in 2% HCl (v/v)) under the optimized collision cell mode gave very low palladium apparent concentrations, in comparison with standard mode analysis. In other words, and as it could be observed in Table 2.4.4, the $^{89}Y^{16}O$ interference was successfully minimized by the 1% NH_3 in He collision gas.

The LOD was calculated as three times the standard deviation of the sample blank solution, and a value of 2.5 ng L^{-1} Pd was found under collision cell mode analysis.

Table 2.4.4. Apparent concentration of palladium due to overlap with YO under standard and collision cell mode analysis

Y concentration, µg L^{-1}	Pd apparent concentration, ng L^{-1}	
	Standard mode	Collision cell mode
1	28.3	5.4
5	116.0	19.7
10	221.6	38.8
50	1128.0	185.9

The feasibility of the proposed method for palladium determination in environmental samples, such as road dust, was checked. The results obtained show a Pd content of 20 ± 2 ng g^{-1} in the road dust sample from the Somport tunnel. The analysis of the certified reference material BCR gave a Pd content of 6.5 ± 1.6 ng g^{-1}, value that was found to be in good agreement with the certified value (6.0 ± 1.8 ng g^{-1}).

In conclusion, the $^{89}Y^{16}O$ spectral interference to ^{105}Pd was successfully minimized by the use of 1 mL min^{-1} 1% NH_3 in He as collision gas. This approach of minimizing the YO^+ interference on ^{105}Pd has the added advantages that additional separation and preconcentration steps are unnecessary.

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2.5 Solid Sampling GFAAS and ICPMS for the Determination of Trace Amounts of Palladium

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2.5.1 Introduction

The great importance of palladium in today's industry and its widespread use make the development of analytical methods that allow the reliable determination of this precious metal in a great variety of samples necessary. However, the determination of this element at trace and ultratrace levels, as often required, may be very challenging.

Sample dissolution for palladium determination is frequently complicated, especially for environmental and geological analysis, requiring time-consuming and cumbersome procedures, frequently involving the use of hazardous reagents (e.g., HF or $HClO_4$) [1-2]. Moreover, even the most sensitive analytical techniques face some difficulties in order to accomplish the determination of palladium at the $\mu g\ g^{-1}$ level and below. Neutron Activation Analysis (NAA) is a powerful technique, but for reliable ultratrace palladium determination the use of pre-concentration/separation steps is necessary [3-4]. Similar comments can be made for atomic absorption (AAS) or optical emission (OES) techniques [1,5,6]. Inductively coupled plasma-mass spectrometry (ICPMS) offers a higher detection power for this element, but the main problem for this technique is the well-documented occurrence of spectral interferences on all palladium isotopes due to the occurrence of isobaric nuclides and molecular and doubly charged ions. Many of these interferences cannot even be spectrally resolved when high resolution-ICPMS is used [7], and the low concentration of the analyte compared to the higher level of the interfering elements in many samples may make the use of separation/pre-concentration steps compulsory [8,9].

Literature on the development of different pre-concentration/separation steps for palladium determination is extensive. The use of selective chelating agents [1,5], ion exchange resins [9,10], electrochemical pre-concentration [11,12], and mercury or tellurium co-precipitation [13,14], are some of the solutions proposed. However, while many of these methods can provide reliable results, they are often time-consuming and may suffer from incomplete recovery and/or contamination problems.

Taking all these factors into consideration, the development of methods that permit the direct determination of palladium in solid samples could be a logical choice to deal with this problem. In this way, it would be possible to improve the sensitivity (by avoiding the dilution that usually accompanies sample digestion), considerably increase the sample throughput (by eliminating the digestion and pre-concentration steps) and reduce the risk of contamination/losses. It is the main goal of this chapter to present information on the current potential of some solid sampling techniques that, according to recent advances reported in the literature, may be well suited for the fast and reliable direct determination of Pd in different samples. The techniques covered in this work include solid sampling-graphite furnace atomic absorption spectrometry (SS-GFAAS), solid sampling-electrothermal vaporization-inductively coupled plasma mass spectrometry (SS-ETV-ICPMS) and laser ablation-inductively coupled plasma mass spectrometry (LA-ICPMS).

2.5.2 Basic operating principle of the techniques discussed

Of the three techniques that are discussed in this work (see Fig. 2.5.1), SS-GFAAS is the oldest one. Direct analysis of solid samples using commercially available graphite furnaces has already been carried out for more than 30 years [15]. However, recent advances in instrumentation may give rise to an increased interest of routine laboratories in this technique [16]. Regarding the principle of operation, the solid sample is weighed and introduced into a graphite furnace that is subsequently subjected to a temperature program in Ar atmosphere. Both temperature and holding time can be controlled. The maximum temperature that can be applied may reach up to 3000 ºC, and the total time per measurement is usually 2-3 minutes. By means of this temperature program, atoms of the target element are produced. These atoms interact with the radiation of a line source (usually a hollow cathode lamp), which emits radiation at the exact wavelengths at which the analyte atoms are capable of absorbing. The absorbance obtained is related to the amount of analyte introduced in the furnace. Typically, samples of approximately 1 mg are analyzed by this technique.

Maybe the main disadvantage of SS-GFAAS is that it is currently a mono-element technique. Therefore, attempts were made to develop a new technique combining the potential of the graphite furnace for the efficient

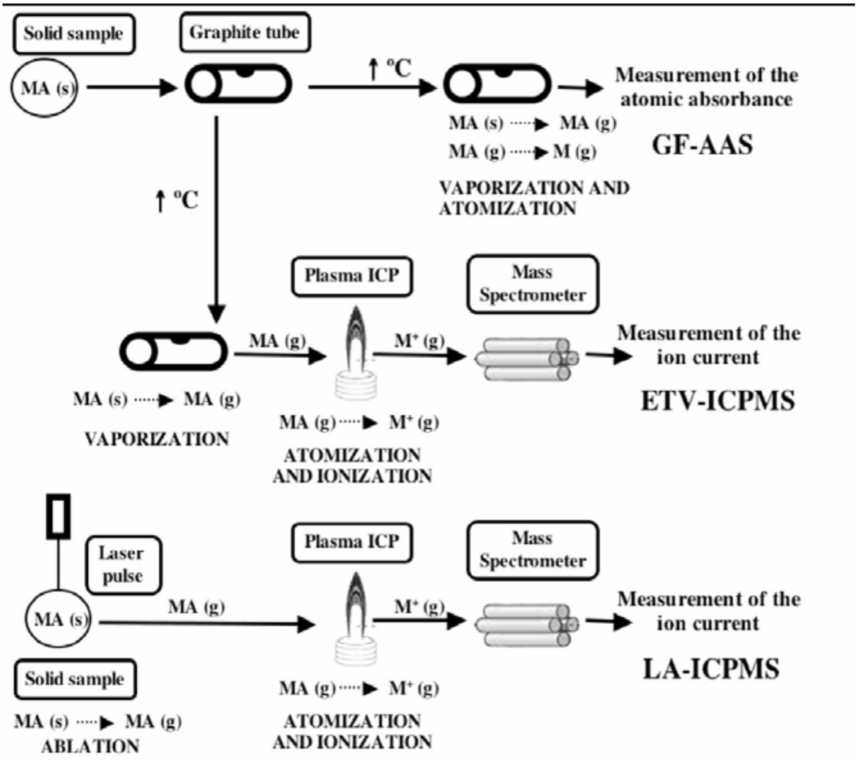

Fig. 2.5.1. Principles of operation of the solid sampling techniques covered in this chapter. M represents the analyte (normally a metal), in the different forms in which it is expected to be found (e.g., in the solid sample, as a salt -MA-)

vaporization of solid samples at a controlled temperature with a more powerful detection system. In this way, ETV-ICPMS was developed, proving its utility for direct solid sampling during the last decade [17]. In this technique, a graphite furnace similar to that used in GFAAS is utilized. However, the goal is only to vaporize the analyte. The analyte atoms or molecules formed in the furnace will be transported into an ICPMS unit for their detection and quantification by means of an Ar flow. The high temperature of the ICP (up to 8000 ºC) ensures the atomization and ionization of the analyte species, and the power of detection of the mass analyzer (in most cases, a quadrupole filter) permits the simultaneous quantification of different isotopes of the analyte or analytes of interest [18].

A different approach, also based on the potential of ICPMS for ultratrace analysis, has received significant attention in the latest years. This technique is known as laser ablation (LA)-ICPMS. The principle of the technique is based on the use of a very short laser pulse (typically a few nanoseconds) that delivers a burst of energy to the sample surface. Upon impact of the beam, a small amount of sample material is ablated and the aerosol thus formed is conducted by a gas flow into the ICPMS instrument, where ionization, detection and quantification occur. When this technique is used, the amount of material that is analyzed is orders of magnitude below that of SS-GFAAS or SS-ETV-ICPMS (μg or less), so it can be considered as a *quasi* non-destructive technique. Moreover, the use of a laser system with a very small spot size (from a few μm to hundreds of μm) allows spatially resolved information to be obtained, both laterally or in depth. As a drawback, it can be mentioned that, for inhomogeneous samples, obtaining a representative value based on the small amount analyzed may be problematic.

2.5.3 Recent developments in the direct determination of Pd solid samples

Possibilities of SS-GFAAS

As indicated previously, SS-GFAAS is a rather old technique. However, only a few applications involving Pd determination have been reported up to date. In 1989, Schmiedel et al. carried out some preliminary experiments to evaluate the possibility for determining Pd as well as other elements (Mo, Ru and Rh) in nuclear fuel cycle waste. However, they pointed out difficulties in handling the samples with their solid sampling system (cup-in-tube set-up) and the slurry procedure was therefore preferred instead [19]. In 1993, Hinds published a paper comparing slurry and direct solid sampling approaches for the determination of Au, Pt and Pd in high purity silver. This author also used the cup-in-tube technique for solid sampling, and pointed out the difficulty in automation as a drawback of the latter method. Calibration was carried out against aqueous standards with a matched amount of dissolved silver in order to minimize matrix effects on the results obtained [20]. The concentration in the sample analyzed was approximately 40 μg g^{-1} and a detection limit of 1.8 μg g^{-1} was reported for the direct solid sampling technique.

In spite of these not very promising previous works, recent advances in instrumentation have resulted in an important progress for the application of SS-GFAAS in real-life analysis. These advances can also result in a considerable improvement for the direct determination of Pd. In this sense, it is fair to indicate that the values previously mentioned were obtained with outdated instrumentation. Most of the negative comments on the difficulty of sample handling and introduction no longer apply to the present situation. Modern SS-GFAAS units may be equipped with a device for automatic weighing and introduction of the solid sample [16]. Moreover, the use of a platform designed for handling higher sample amounts and the transversal heating of the graphite tube, resulting in a more homogeneous temperature distribution, are also improvements worth to mention.

Resano et *al.* have recently evaluated the capability of present SS-GFAAS instrumentation for palladium determination in different samples. Three samples of very different characteristics and different palladium content were selected for this study: a pharmaceutical drug (enalapril maleate), a polymer ("Carilon") and a reference material (NIST SRM 2556, used auto catalyst) [21].

One of the main advantages of the approach is related with the potential of the graphite furnace to use the temperature program in order to minimize possible matrix effects. In theory, by controlling the temperature (the use of chemical modifiers may further extend this possibility), it could be possible to separate in time the atomization of the analyte from the vaporization of most matrix components. If this is achieved, straightforward calibration with aqueous standards should be possible [22]. In this particular case, direct determination of Pd in samples of organic nature is very simple. Palladium is not a very volatile element, resisting pyrolysis temperatures of up to 1200° C without significant losses. At this pyrolysis temperature, most of the organic material present in the samples can be efficiently removed, leaving the analyte in the graphite furnace for subsequent atomization (at 2400 ºC). Hence, Pd determination in both "Carilon" and Enalapril maleate was shown to be viable. In both cases, the most sensitive atomic line of 247.6 nm was used and calibration against aqueous standards was feasible. The concentration of Pd in the "Carilon" sample ($\approx 7\ \mu g\ g^{-1}$) posed no special difficulty (in fact, an Ar mini-flow was maintained during atomization in order to reduce the sensitivity), but the situation for enalapril maleate was more complex. Palladium is present at a very low level in this sample ($\approx 2\ ng\ g^{-1}$), very close to the detection limit of the technique when typical sample masses of a few milligrams are analyzed. In order to overcome this problem, a fast *in situ* pre-concentration procedure was proposed. This procedure consisted of depositing a high sample amount onto the platform (7 –

10 mg), carrying out the drying and pyrolysis step for efficient matrix removal and adding more sample again. By repeating this procedure 5 times a total sample mass of 35-45 mg was sequentially pyrolized, and the total palladium content was pre-concentrated onto the platform and subsequently submitted to the atomization step. In this way, a palladium signal above the quantification limit was obtained. This procedure resulted in a detection limit of 0.4 ng g^{-1}.

The direct analysis of the inorganic sample -NIST SRM 2556- presented more complications *a priori*. The main component of this material is Al_2O_3, which can hardly be vaporized during the pyrolysis step. Therefore, the opposite approach was attempted: Palladium could be atomized again at 2400ºC, a temperature at which most of the matrix still remains in the furnace (these residues were mostly removed during the cleaning step at 2700 ºC), producing only a moderate background that can be efficiently corrected for (the instrument is equipped with Zeeman-effect for background correction). The signal for the solid sample was delayed compared with the signal obtained for the aqueous standards, a situation frequently encountered when the direct atomization of an analyte from a refractory inorganic matrix is aimed at [23]. However, the relevant aspect is that both peak areas are comparable, as shown in Fig. 2.5.2, enabling again the use of aqueous standards for calibration. In this particular case, the Pd content was fairly high (326 µg g^{-1}), and the use of a less sensitive atomic line (311.4 nm) was necessary for successful determination.

As a conclusion it can be stated that the use of modern SS-GFAAS permits the direct determination of Pd in solid samples of very different nature and at very different concentrations (from the low ng g^{-1} to the high µg g^{-1} levels). This element presents plenty of alternative non-resonance lines in order to adjust the sensitivity when necessary. In the cases studied, direct calibration against aqueous standards was feasible, resulting in excellent accuracy (agreement with the corresponding reference values better than 3%). Every determination consisted of the measurement of five solid samples (approximately 15-20 minutes of work) and the median of the five was taken as representative value, in order to minimize the possible influence of outliers [24]. The exception to this working procedure was the analysis of Enalapril maleate, since, with the preconcentration procedure used, only one value per determination was obtained. The precision obtained depended to a great extent on the concentration level and sample mass used. RSD values were between 3 (for NIST 2556, a very homogeneous sample with a high Pd content) and 15% (for Enalapril maleate, which can be considered as acceptable taking into account the low Pd content in this sample).

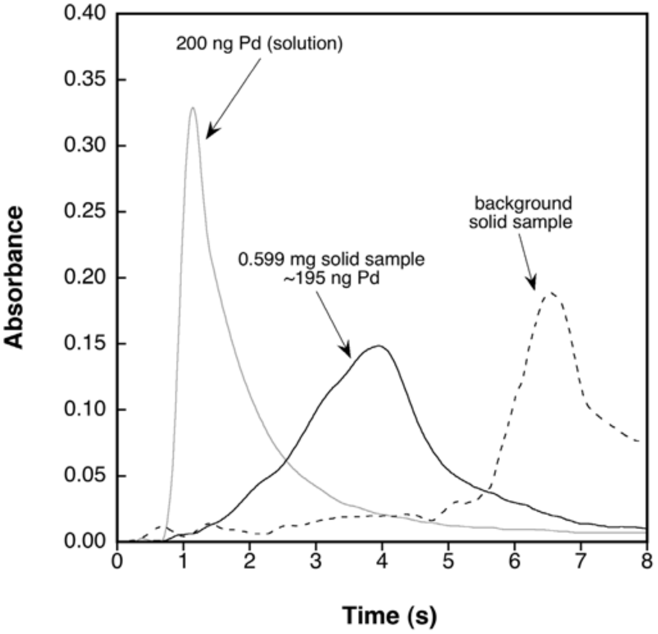

Fig. 2.5.2. Comparison of the signal obtained for atomization of Pd from a solid sample (NIST SRM 2556) and from an aqueous standard. 10 µl solution (200 ng Pd) Q_A= 0.390 s; 0.599 mg solid sample (195 ng Pd) Q_A=0.382 s

Overall, the technique performance seems to be very promising and the future development of fast procedures for the determination of Pd in solid samples of various origin and composition can be expected.

Possibilities of ETV-ICPMS

In spite of the potential of SS-GFAAS for Pd determination, one of the drawbacks of this technique is the lack of multi-element possibilities. This aspect may change in the future, as some work on the development and applications of multi-element GFAAS has been and still is carried out [25]. The coupling of an electrothermal device to an ICPMS unit is an interesting alternative, adding the high sensitivity, isotopic information and multi-element possibilities offered by ICPMS to the temperature control and ability to handle solid samples of the graphite furnace. This combination may thus be of great interest, especially for those situations in which determination of various elements is needed.

However, only a few papers have reported on this technique for direct determination of Pd so far. In 1995, Lüdke et al. described a singular system for the direct determination of Pt, Pd Rh and Ir in automotive catalyst exhausts [26]. The samples originated from a gasoline driven engine equipped with a standard three-way catalyst, running on a computer controlled dynamometer. The particulates containing these elements were fractionated according to their size and collected on separate impaction targets (small flat discs made of pure graphite with a diameter of 4 mm and a thickness of 2 mm). These graphite targets were directly inserted into specially modified graphite tubes and submitted to a suitable temperature program for their analysis by means of ETV-ICPMS. The high sensitivity of the method developed (limits of detections of 0.1 pg were reported) allowed the determination of the elements of interest in spite of their low content (0.3 ng/m^3 for Pd). The correlation between the different elements was studied, leading to the conclusion that Pd and Ir particles originated from a different source than the Pt and Rh particles.

In a later paper, Vanhaecke et al. studied the potential of ETV-ICPMS for palladium determination in "Carilon" (a solid aliphatic polyketone) [27]. This sample is a polymer identical to that studied by means of SS-GFAAS [21], although with a slightly different Pd content. As indicated previously, this kind of sample is simple for graphite furnace analysis since the matrix can be easily removed during the pyrolysis temperature without Pd losses, and, therefore, few matrix effects can be expected. Different calibration approaches were evaluated in this work. It could be concluded that aqueous standards can be used for calibration but an internal standard is needed in order to correct for possible sensitivity drifts during the analysis. The signals of $^{80}Ar_2^+$ or $^{193}Ir^+$ (that has to be added for this purpose) were both appropriate as internal standards, although the use of Ir deteriorated the detection limit (from 1 pg to 20 pg, which corresponds with 1 ng g^{-1} and 20 ng g^{-1}, respectively, for a typical sample mass of 1 mg) as a result of contamination of the Ir stock used. In any case, these detection limits could be further improved since the authors used the Omni Range device to selectively decrease the sensitivity (the Pd content in the sample was of approximately 5 µg g^{-1} leading to too high a signal otherwise). Therefore, the detection limit reported in the previous work (0.1 pg, corresponding to 0.1 ng g^{-1} for a sample mass of 1 mg) can be considered as a better estimation of the real potential of this technique.

Maybe the most important problem for the determination of low Pd levels when using ICPMS is the occurrence of spectral interferences. These interferences are due to i) the formation of polyatomic ions; ii) the occur-

Table 2.5.1. Isobaric, molecular and doubly charged ions potentially hampering accurate determination of Pd, Pt and Rh (non-restrictive selection)

Analyte nuclide (isotopic abundance)	Potentially interfering ions
^{103}Rh (100%)	$^{206}Pb^{2+}$, $^{87}Sr^{16}O^{+}$, $^{87}Rb^{16}O^{+}$, $^{40}Ar^{63}Cu^{+}$, $^{36}Ar^{67}Zn^{+}$
^{104}Pd (11.1%)	$^{104}Ru^{+}$, $^{40}Ar^{64}Zn^{+}$, $^{88}Sr^{16}O^{+}$, $^{208}Pb^{2+}$
^{105}Pd (22.3%)	$^{40}Ar^{65}Cu^{+}$, $^{89}Y^{16}O^{+}$
^{106}Pd (27.3%)	$^{106}Cd^{+}$, $^{40}Ar^{66}Zn^{+}$, $^{90}Zr^{16}O^{+}$
^{108}Pd (26.5%)	$^{108}Cd^{+}$, $^{40}Ar^{68}Zn^{+}$, $^{92}Zr^{16}O^{+}$, $^{92}Mo^{16}O^{+}$
^{110}Pd (11.7%)	$^{110}Cd^{+}$, $^{40}Ar^{70}Ge^{+}$, $^{40}Ar^{70}Zn^{+}$, $^{94}Mo^{16}O^{+}$, $^{94}Zr^{16}O^{+}$
^{194}Pt (32.9%)	$^{178}Hf^{16}O^{+}$, $^{177}Hf^{16}OH^{+}$
^{195}Pt (33.8%)	$^{179}Hf^{16}O^{+}$, $^{178}Hf^{16}OH^{+}$
^{196}Pt (25.3%)	$^{180}Hf^{16}O^{+}$, $^{179}Hf^{16}OH^{+}$

rence of isobaric interferences from isotopes of other elements; iii) the occurrence of doubly charged ions. A list of the possible interferences for Pd is presented in table 2.5.1.

It has to be mentioned that, in most environmental samples, the concentration of Pd may be orders of magnitude below the concentration of many of the elements giving origin to interfering ions (parent elements), therefore leading to severe problems. The use of ETV as a sample introduction system may help to overcome many of these problems. On the one hand, since a dry aerosol is introduced into the ICPMS instrument, the formation of (hydr)oxide-based polyatomic ions is greatly reduced. On the other hand, the vaporization of Pd can be separated to some extent from the vaporization of some of the parent elements showing a different volatility (e.g., Zn, Pb or Cd are much more volatile than Pd). These aspects were illustrated in a recent paper [28]. Pd was not determined in this work, but Pt and Rh (elements showing a very similar thermochemical behaviour as well as analogous problems regarding interferences, as shown in table 2.5.1) could be simultaneously determined in different environmental samples (road dust -BCR CRM 721-, grass and atmospheric aerosol collected on a cellulose filter) at the ng g^{-1} level and even below (LODs of 0.35 ng g^{-1} for Pt and 0.05 ng g^{-1} for Rh were reported).

It can be concluded that more applications are needed, but SS-ETV-ICPMS may offer unmatched possibilities for fast simultaneous determination of Pd and other PGE (platinum group elements) at the μg g^{-1} and ng g^{-1} level.

Possibilities of LA-ICPMS

Of all the solid sampling techniques discussed in this chapter, this is the one for which most applications concerning the determination of Pd, and other PGEs, have been reported, the majority of them dealing with geological samples. A review on such applications has been recently published [29], therefore the goal of this section would be to present some general information and new features, rather than provide an extensive coverage.

The use of laser ablation as a sample introduction system presents important benefits but also significant disadvantages when compared with the previously mentioned techniques. In this technique it is not possible to separate the ablation of the analyte from that of the matrix, therefore all the material is simultaneously directed into the plasma. As a result, more matrix effects (and spectral interferences) can be expected, and direct calibration with aqueous standards is very complicated. Therefore calibration is usually carried out using matrix-matched standards [29], and the use of an internal standard is often necessary to correct for possible differences in the masses ablated for the sample and for the standards [30].

However, in spite of the difficulties expected if no suitable material is available for calibration, a situation in which reliable quantification may be even precluded [31], the technique also presents very interesting features, such as its potential for spatially resolved analysis (with a lateral resolution of 5 μm and a depth resolution below 1 μm) and for obtaining information on the microhomogeneity of the sample. In this way, it is possible to study the analyte content of discrete particles or inclusions, and some of the publications concerning Pd have taken advantage of these abilities. Of course the technique also shows a good sensitivity and the multi-element capabilities typical of ICPMS.

As an example of this potential, Rauch et al. could identify and track individual particles released from automobile catalysts present in environmental particulates and sediments [32]. The authors indicate that the associ-

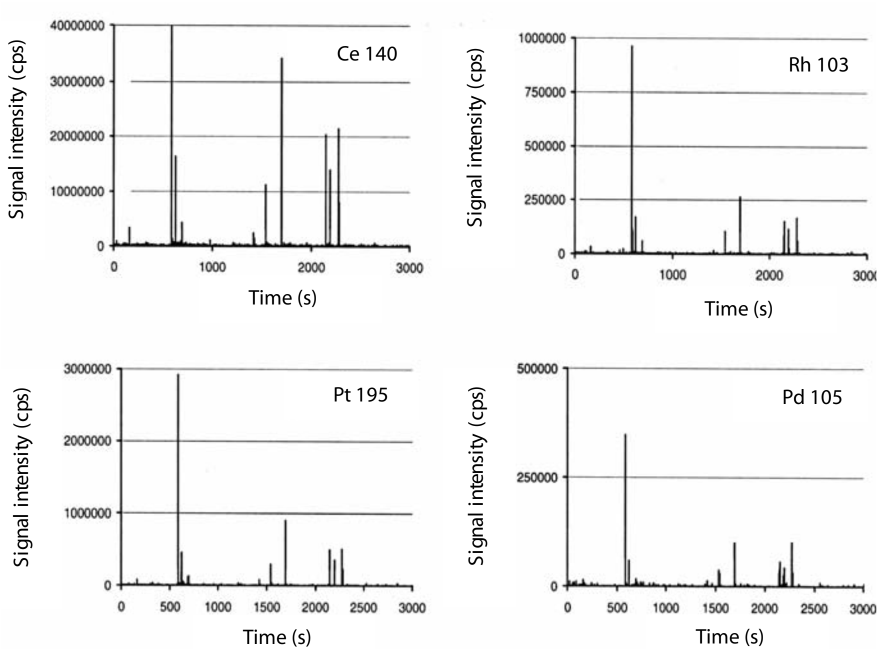

Fig. 2.5.3. Scanning Laser Ablation-ICPMS signals of Ce, Pt, Pd and Rh across gasoline exhaust particles showing their association [32]

ation between Pt, Pd, Rh and Ce (see Fig. 2.5.3) provides a definitive fingerprinting for tracking catalyst particles [32,33], while the relative PGE signal intensity is an indication of the catalyst type. Some of the authors of the previous papers also studied the laser ablation signals of PGEs in bird' feathers and found its very heterogeneous distribution a strong indication of external contamination [34]. Reports on the use of LA-ICPMS for PGE detection in different phases of geochemical samples (e.g., meteorites [31,35]) also prove the usefulness of the technique in this field.

In all the applications mentioned above, obtaining quantitative results was not a requisite, since meaningful conclusions could be obtained on the basis of qualitative information or by measurement of the relative signal intensities of different analytes.

In order to obtain quantitative bulk information, apart from the problem of finding an adequate standard, also the effect of potentially interfering polyatomic ions has to be taken into account. When a laser ablation system is used for sample introduction, a dry plasma is obtained (as with ETV) and the signal intensity of all O- and OH- based molecular ions is reduced. However, the potential of ETV to additionally separate in time the vaporization of the analytes from that of some interfering species based on their different volatility does not exist here. In this sense, Motelica-Heino *et al.* have evaluated the use of LA-ICPMS for bulk analysis of road sediments. The conclusion of the study was that a good accuracy is achievable for Pt and Rh, but unfortunately, that was not the case for Pd, even if high resolution-ICPMS instrumentation was used [36].

Fortunately, some improvements in this direction have been reported recently. Petibon *et al.* have evaluated the potential of a Ne ICP for LA-ICPMS experiments [37]. In spite of the lower sensitivity achieved with this kind of plasma, the detection limits for Pd and also for Rh were improved. This is owing to the reduction in the interference of the Ni and Cu argides on this light PGE (see Table 1) and also to a lower oxide formation level. However, the success of this approach is limited by the high cost of the Ne gas supply.

A more realistic approach is based on the use of a reaction or collision cell. In this approach an additional cell (containing a quadrupole, hexapole or octopole set-up, depending on the manufacturer's design) is introduced in-between the plasma source and the mass analyzer. This cell is filled with a gas, enabling ion-molecule reactions to proceed. The idea is to select an adequate gas so it can react with the interfering ions and remove them, while the analyte should not be negatively affected by its presence. Alternatively, the analyte element could be transformed into a reaction product ion, which can be measured interference-free at another mass-to-charge ratio. Examples of this technology applied to PGE determination can be found in the literature [38,39]. Focusing on LA-ICPMS approaches, Mason and Kraan showed a small attenuation of spectral interferences for Pd and Rh determination in sulfide materials when a collision cell filled with H_2 was used [40]. The authors recognize that the interferences produced for that kind of material were not extreme and only a slight improvement could therefore be observed.

Perhaps a more spectacular example has been recently published by Vanhaecke *et al.* [41]. The authors studied the capabilities of LA-ICPMS for fast and direct determination of Pd, Pt and Rh in Pb buttons. These samples were produced via the fire assay technique, used for preconcentration of PGEs from South-African platiniferous ores. Of course, carrying out the direct analysis of the Pb buttons would result in important benefits compared with the laborious digestion approaches alternatively needed. In this particular case, preparation of matrix-matched standards for suitable calibration was relatively simple and the signal of $^{204}Pb^+$ could serve as an appropriate internal standard. However, the determination of Rh was affected by the occurrence of the $^{103}Rh^{+}/^{206}Pb^{++}$ overlap, which is especially severe in a Pb matrix. The authors proved that the used of NH_3 as a reaction gas permitted the resolution of this interference while not negatively affecting the simultaneous determination of the other analytes (Pd and Pt). Detection limits below 100 ng g^{-1} were reported for all the analytes of interest.

From the results presented, it can be concluded that the use of collision/reaction cell-based ICPMS instruments may allow the development of suitable methods for the determination of Pd, and also other PGEs, in many samples for which is was not possible to achieve reliable results up to date.

2.5.4 Conclusions

This chapter reviews the most recent developments concerning the use of SS-GFAAS, SS-ETV-ICPMS and LA-ICPMS for palladium determination. The application of SS-GFAAS may be beneficial considering the low detection limits (below ng g^{-1}) that can be achieved, the high sample throughput (15-20 minutes per sample) and the possibility to calibrate using aqueous standards. The use of SS-ETV-ICPMS can further extend this potential owing to the higher detection power and the possibility of simultaneous monitoring of other analytes, since often determination of Pt, Rh and/or Au is also required in many samples.

Finally, the use of LA-ICPMS offers additional possibilities to study the distribution of the analyte in the sample and its association with other elements in the particles or inclusions of interest. For quantitative bulk analysis, however, the method relies on the use of solid matrix-matched standards or, at least, on the availability of a suitable internal standard. On the other hand, the development of collision/reaction cell-based methods can greatly help to improve the problems encountered with this technique, owing to their ability to successfully cope with spectral interferences.

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2.6 Preconcentration and Separation Methods for the Determination of Trace Palladium in Environmental Samples

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2.6.1 Introduction

Palladium is an element of increasing importance in today's industries. Due to the catalytic properties it is widely used in the synthesis of many materials, from polymers to pharmaceuticals. In addition to this, its emission from the automotive catalytic converters has resulted in an increase in the concentration of palladium in the environment. An elevated level of Pd compared to geochemical background (Helmers et al. 1998) has been found in airborne particulate matter (Tilch et al. 2000), road dust (Boch et al. 2002; Kovacheva and Djingova 2002; Leśniewska et al. 2004), soil (Patel et al. 2000; Ravindra et al. 2004) and grass (Schuster et al. 1999). Van de Velde et al. (2000) presented comprehensive data on the occurrence of Pd in alpine ice and snow dating from the late 18th century to the early 1990s. Increasing palladium content in the samples collected at a high-altitude location near the summit of Mont Blanc was detected, particularly over the last decade.

The monitoring of Pd in environmental samples has great importance with respect to estimation of the future risk of the human health and the ecosystem. Palladium analysis requires analytical methods of high sensitivity, selectivity and the control of interference effects. The most widely used methods for determination of Pd in environmental samples include graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma mass spectrometry (ICP-MS) and adsorptive stripping voltammetry (ASV). Despite the high sensitivity, ICP-MS requires appropriate choice of sample introduction technique, preferably one possessing the option of solid sample introduction (Kántor, 2001). Moreover, spectral and non-spectral interferences could cause several difficulties in the correct determination. Riepe et al. (2001) proposed chemically modified sample introduction capillary to remove the interfering elements for the determination of Pd by ICP-MS. The strong cation-exchanger (2-(4-chlorosulfonylphenyl)-ethyltrichlorosilane), covalently bound to the silica capillary, can retain Cu^{2+} and YO^+ during sample introduction, whereas palladium breaks through the capillary and can be determined in the absence of interfering matrix constituents. Other sensitive techniques such as neutron activation analysis (NAA) or total reflection X-ray fluorescence spectrometry (TXRF) are less often applied due to the complexity and cost of the required instrumentation. It should be remarked that for palladium determination by NAAA detection capability is limited due to strong interference of bromide, mainly ^{82}Br, which is present in almost all organic matrices in the ultra trace range (Schwarzer et al. 2000). The analytical methods for the determination of palladium as well as other platinum group elements have been recently reviewed (Rao and Reddi, 2000; Bencs et al. 2003; Barefoot, 2004)

In environmental samples, the low concentration of palladium (nanogram per gram levels) together with the high concentration of interfering matrix components often requires an enrichment step combined with a matrix separation. Fire-assay, coprecipitation, solvent and solid phase extraction techniques have been developed and applied for preconcentration and separation of palladium prior its detection. An alternative approach may be based on the electrodeposition to avoid matrix interferences. The selection of a suitable enrichment procedure depends considerably on the palladium concentration and the method for its final determination.

The preconcentration procedures are executed for off- or on-line systems. Application of off-line enrichment is adequate when higher preconcentration factors are needed. However, these procedures require a great amounts of reagent and samples. When on-line systems are condidered, the main advantage is the possibility of automation which increases precision and accuracy. Further, it reduces the risks of sample contamination. Detailed information reffering to on-line preconcentration systems coupled to atomic spectrometry can be obtained from the literature (Burguera and Burguera, 2001; Alonso et al. 2001).

2.6.2 Coprecipitration

Reductive coprecipitation with a suitable collector can be applied for enrichment of trace palladium and its separation from other elements. The procedure with mercury was particularly optimized for Pd determination by TXRF (Messerschmidt et al. 2000, Sures et al. 2001). Reduced palladium as well as gold exhibit high solubility in mercury, whereas the solubility of platinum is much lower. Collector can be then effectively removed from the sample by evaporation at 300^{O}C. Formic acid was selected as the most suitable compound for reduction as it reacts with formation of only H_2O and CO_2. However, the proposed method is time consuming and may serve mainly as an independent method in order to control other analytical techniques.

Coprecipitation with tellurium for the simultaneous determination of Pt, Pd and Rh by ICP-MS in environmental samples (Gòmez et al. 2003) and some geochemical reference materials (Sun et al. 1998) have been proposed. Application of the isotopic dilution method improved the results obtained for road dust samples.

Fire assay technique with lead buttons (Vanhaecke et al. 2004) or nickel sulfide (Sun et al. 1998) can collect palladium from relatively large samples with complex matrices. The high reagent blank was found, mainly from the nickel oxide. Thus, it should be carefully purified before use.

Liquid-liquid extraction

Liquid-liquid extraction is widely used technique for separation and preconcentration of platinum metals, including palladium, due to its simplicity and despite disadvantages such as laborious manipulation or possibility of emulsion formation. Patel et al. (2000) proposed the method based on the formation of Pd(II)-$SnCl_3^-$-N-butylacetamide complex followed by its extraction with 1-pentanol. This method with GFAAS detection was applied for determination of palladium in soil samples. The formation of the ion-pair between anionic complex of $Pd(SCN)_4^{2-}$ and cationic potassium complex of dicyclohexyl-18-crown-6 in hydrochloric acid media has been proposed for separation of palladium from Pt and Rh (Hossain and Honjo, 2000). The formed product was extracted into chloroform and then re-extracted as $Pd(NH_3)_4^{2+}$and determined by FAAS.

For determination of palladium in copper ores by GFAAS extraction of its dimethylglyoxime complex into chloroform has been performed (Brzezicka and Szmyd, 1999). To prevent errors caused by the high volatility of $CHCl_3$, the organic extracts were evaporated to dryness with the mixture of HCl-HNO_3 (3:1) and then the dry residue was dissolved in diluted hydrochloric acid solution. However, copper, iron as well as lead present in the sample matrix are partially coextracted with Pd by this procedure.

Efficient preconcentration method is cloud point extraction where immiscible liquid phase separation can be achieved by varying the temperature of a monophase system (Sanz-Medel et al. 1999). The surfactant molecules, when their specific concentration is achieved, could formed micscelar structures. These structures are able to associate with metal ions and their chelates. Cloud point extraction technique was applied for separation and preconcentration of Pd, Pt, Rh, Ru and Au with *O,O*-diethyldithiophosphate as a complex forming agent and Tritition-114 non-ionic surfactant (da Silva et al. 2001). By increasing the temperature up to so-called cloud point, a phase separation occurs, resulting in the surfactant-rich phase containing analyte complexes. Since the volume of the surfactant can be very small, high enrichment factors can be obtained. This enrichment was utilised for ICP-MS determination in biological matrices.

Solid-phase extraction

Among the numerous techniques reported for preconcetration and matrix separation of palladium, the methods using sorbent extraction have proved to especially effective (Pyrzyska, 1998; Godlewska-Żyłkiewicz, 2004). Chlorocomplexes of palladium exhibit high affinity for strong basic anion-exchange resins with stryrene or acrylic polymers cross-linked with divinylbvenzene which can be applied for enrichment of Pd from a large volume of HCl solution (Matsubara et al. 2000; Kovacheva and Djingova, 2002). However, other elements which form anionic complexes during digestion procedures for environmental samples, could be also preconcentrated on such resins. Iron, strontium, copper and molybdenum ions were retained on anionic resins (Hann et al. 2001; Kovacheva and Djingova, 2002). Also sorption of Zr(IV) on Dowex 1x8 resin caused problems during determnination of Pd by ICP-MS due to severe spectral interferences (Meisel et al. 2001).

Cellulose-based sorbents with weak anion exchange groups and fiber structure show moderate affinities towards palladium as well as other noble metals. This can be a factor facilitating their quantitative recovery (Brajter and Słonawska, 1989; Levai et al. 1998; Godlewska-Żyłkiewicz et al. 2000). The retained metals can easily be eluted from the column with dilute thiourea. Eluents containing thiourea are preferably utilised in desorption not only for cellulose anion exchangers but also from a few chelating resins (Shah and Devi, 1997; Liu et al. 2000; Zhang et al. 2002; Chwastowska et al. 2004).

Vlašànkova et al (1999) applied a modified silica gel ($C_{18)}$ for the separation and preconcentration of platinum metal ions as ion association (pairing) complexes with the cation of onion salt of *N*-(1-carbaethoxypentadecyl)-trimethyl ammonium bromide prior to ICP-AES and ICP-MS determination. The suitability of acidic form of activated alumina for on-line palladium preconcentration/elution and final determination by ICP-MS was investigated by Moldovan et al. (2003). The proposed system allows removal of the primary ^{105}Pd interferences (Cu and Y) using KCN solution as an eluent. Sorption of Pd, Pt and Rh complexes formed on-line with diethylthiourea on the inner walls of a PTFE knotted reactor has been also proposed (Bnkhedda et al. 2003). A quantitative elution was done using small volume of methanol acidified with HNO_3. Fully automated on-line system for preconcentration of palladium was accomplished on C_{18} microcolumn modified with a strong determination (Schuster and Schwarzer, 1996). From a 5 ml sample solution, a 200-fold sensitivity enhancement was obtained.

Recently, quantitative enrichment of palladium from dilute aqueous solutions was achieved with ion printed polymer particles prepared by using Pd-dimethylglyoxime-vinylpiridine ternary complex as template and by thermally copolymerization with styrene and divinylbenzene in the presence of 2,2`-azobisisobutyronitrile as initiator (Daniel et al. 2003). Palladium was eluted completely by stirring for 15 with 2x10 ml of 50% (v/v) HCl. This material showed much higher selectivity towards Pd over Pt and other metals (Cu, Zn and Ni) compared to recognition (blank) polymer.

Material of biological origin such as fungi, algae and bacterial biomasses have been extensively studied for the uptake and recovery of some metals including palladium (Perez-Corona et al. 2001; Godlewska-Żyłkiewicz, 2001,Guibal et al. 2001). The retention of metals by biomass can take place by bioaccumulation or biosorption and involves ion-exchange, adsorption, complexation and precipitation processes occurring on the cell wall. Immobilization of cells on controlled pore glass or silica gel improves their mechanical properties and enables to regenerate biosorbent. Sorption properties of natural biopolymers can be improved by grafting new functional groups onto the natural backbone. Guibal et al. (2002) found that rubeanic acid derivative was more 4efficient for the uptake of Pd from dilute solution in comparison to thiourea derivatives of chitosan. Inexpensive baker's yeast and green algae have been showed selective accumulation of Pd and Pt from water samples in acidic medium (Godlewska-Żyłkiewicz, 2003). Biosorption of these metals on algae covalently immobilized on silica gel could be realised in a flow mode.

Electrochemical preconcentration

This preconcentration purpose is based on electrolysis principles, in which the electric current passing through an electrochemical cell allows the occurrence of chemical reactions in a system containing electrodes. Komárek et al. (1999) proposed electrodeposition of Pd and Pt onto the inner surface of pyrolytically coated graphite tube, which subsequently served as an atomizer for GF AAS measurements. However, corrosion of the tubes was observed due to penetration of the acidic sample solution into the graphite. It seriously reduces the lifetime of the pyrolytically coating.

Similar electrodeposition method was employed for determination of Pd, Pt, Rh and Ru by GFAAS in dust samples (Matusiewicz and Lesiński, 2002).

Ohta et al. (1997) proposed enrichment of palladium from spiked river and seawater samples in electrochemical Mg-W cell. A spontaneous redox reaction between Pd and magnesium sheet was used to provide a voltage and an electron flow. The tungsten sheet with deposited analyte was further employed as a W-tube atomizer.

An electrochemical palladium preconcentration on a glassy carbon electrode at a controlled potential was performed in a flow-through cell prior to its GFAAS determination (Godlewska-Żyłkiewicz and Zaleska, 2002). After electrolysis the polarization of the electrodes was changed and deposited metal was dissolved in the presence of acidic thiourea solution. This method could be applied for analysis of natural waters. However, additionally UV irradiation is needed due to strong adsorption of organic compounds at the electrode surface.

2.6.3 Conclusions

The importance of palladium has increased greatly as a result of technological developments in catalyst for industries and catalytic converters for automobiles. Until now, its compounds have little impact on the environment. However, some areas such as roadsides have experienced increasing Pd contamination during recent years. Atomic spectrometry techniques, used mainly for determination of palladium in such samples, present limitations related to sensitivity or selectivity. Application of preconcentration/separation procedures is able to minimise these problems in an elegant way. The recent developments in this area was discussed an the applied procedures based on coprecipitation, liquid-liquid and solid phase extraction as well as electrochemical principles were presented.

In order to judge the actual risk of palladium in environment and to understand its transformation, methods for the determination of palladium species need to be developed. So far no papers concerning speciation analysis of Pd in environmental samples, in contrast to platinum, have been published. Th4e analytical methods for such studies can be developed using hyphenated techniques such as coupling high performance liquid chromatography or capillary electrophoresis with a sensitive detection system as mass spectrometry.

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2.7 Analytical Problems and Validation of Methods for Determination of Palladium in Environmental Materials

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2.7.1 Introduction

The introduction of platinum metals-based automotive catalytic converters on a large-scale opened a new chapter in the environmental analytical chemistry – determination and monitoring of Platinum Group Elements (PGEs) in the environment. The intensive traffic in the last two decades resulted in significant increase of PGEs concentrations (Bencs et al. 2003) which exceed up to 3 orders of magnitude their natural abundance (Hartley 1991). This might become stressful to the biosphere and requires investigation and elucidation of PGE accumulation and distribution in nature.

Platinum is the most investigated element among the PGEs-pollutants (e.g., Balcerzak 1997, Lustig 1997, Hees et al. 1998, Helmers and Kümmerer 1999, Zereini and Alt 2000, Bencs et al. 2003). This is mainly due to its highest release and subsequent accumulation in the environment.

Among the other PGE Pd and Rh became of special interest as part of catalytic converters and their rapidly increasing concentrations in the last few years (Ravindra et al. 2004). In 1998 Helmers et al. (1998) pointed that palladium-based catalysts may more and more constitute a main source for Pd in the environment. Five years later Pt is increasingly replaced by Pd (Gómez et al. 2003) which consumption for catalyst production in 2002 has been about 12 times higher than in 1993 (Zereini et al. 2004). Therefore having in mind the highest bioavailability of Pd among PGE (Schäfer et al. 1998) and its cytotoxicity and mutagenic effects in living organisms (Gómez et al. 2003) the need for reliable methods for analysis and the necessity for its determination in environmental samples becomes obvious.

The problems in the determination of Pd in environmental samples are similar to that of Pt namely very low environmental concentrations and lack of appropriate Certified Reference Materials (CRMs) for validation of the methods. In the case of Pd however the situation is still worse due to higher spectral and non-spectral interferences which limit the possibilities of the methods usually applied for analysis of PGE. Thus the measurement of Pd by electrochemical methods (very common in the case of Pt) is rather complicated due to the irreversibility of the electrode processes (Georgieva and Pilar 1997). The determination of Pd by Instrumental neutron activation analysis (INAA) demands working at the nuclear reactor facility and using short irradiation and cooling times (due to the very short half life of the nuclides) (Heinrich et al. 1996) and such possibilities are very few keeping in mind that a lot of research reactors have been shut down during the last decade. Quadrupole inductively coupled plasma mass spectrometry (Q-ICP-MS) has serious problems in the instrumental determination of Pd due to interferences from a lot of elements (Zr, Y, Mo, Cu, Sr etc.) having higher concentration in environmental matrices than Pd. Even Isotope dilution inductively coupled plasma mass spectrometry (ID-ICP-MS), Sector field inductively coupled plasma mass spectrometry (SF-ICP-MS) and High resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) are not always able to solve these interferences (e.g., Köllensperger et al. 2000, Bencs et al. 2003, Fritsche and Meisel 2004). Therefore in most cases separation and preconcentration methods are developed before measurement. The "classic" separation and concentration method for PGE is Ni-fire assay however it is not always suitable for environmental samples (Bencs et al. 2003) The complex formation with N,N-diethyl-N'-benzoylthiourea is recognized as a very sensitive way for concentration of Pd (Schuster and Schwarzer 1996) but the reagent is not commercially available. Table 2.7.1 presents some of the methods used for Pd determination in soils, sediments and plants and information about specific separation and preconcentration procedures depending on the matrix and method. Only papers are included where the method information is described in details.

Significant efforts are spent for development of methods for Pd determination in various environmental matrices: mostly road dust (Boch et al. 2002, Godlewska-Żyłkiewicz and Zaleska 2002, Kovacheva and Djingova 2002, Matusiewicz and Lesiski 2002, Djingova et al. 2003b, Gómez et al. 2003), soils (Zereini et al. 1993, Heinrich et al. 1996, Zereini et al. 1997a, Schäfer et al. 1998, Schäfer et al. 1999, Ely et al. 2001, Fritsche and Meisel 2004) but also airborne particles (Gómez et al. 2003, Zereini et al. 2004) sewage sludge (Helmers et al. 1998, Schäfer et al. 1999) and plants (Kothny 1987, Lee et al. 1993, Schäfer et al. 1998, Ely et al. 2001, Djingova et al. 2003b).

In spite of the efforts for reliable determination of Pd still the quality of the data in the literature is considered unsatisfactory mainly due to lack of errors provided with the data, insufficient use of direct methods for comparison (Ely et al. 2001) and the lack of suitable CRMs for environmental analysis.

The preparation of BCR-723 for the quality control of Pd, Pt and Rh in road dust (Zischka et al. 2002) led to the solution of the validation problems in the analysis of samples of this often investigated material. However the lack of appropriate CRMs, needed when soils, sediments and plants are analyzed (not to mention biomedical samples and water), is a serious obstacle when accuracy and precision of the applied methods are to be evaluated. Table 2.7.1 presents the most common solutions of this problem.

The aim of the present paper is to demonstrate the validation process in the determination of Pd in environmental matrices (road dust, sediments, plants, etc.) using the three methods we have developed based on ICP-MS, ICP-AES and High performance liquid chromatography (HPLC).

Table 2.7.1. Methods for analysis and validation of Pd in soils and plants

Determined PGE	Sample Matrix	Sample Digestion Method	Separation /preconcentration	Instrumental technique	Method validation	Reference
Pd, Pt, Rh	Urban dust, Road dust, Soil, Sewage sludge; Airborne dust	Wet chemical digestion	NiS fire assay; Te-coprecipitation	Q-ICP-MS, HR-ICP-MS	CRMs: SARM-7 and WPR-1; Independent method: Graphite furnace atomic absorption spectrometry (GFAAS)	(Schäfer et al. 1999)
Pd, Pt, Rh, Ru, Ir	Soil, Sediment, Tunnel dust; Surface waters	Wet chemical digestion; Leaching; High pressure asher (HPA)	NiS fire assay	GFAAS, X-ray fluorescence spectrometry (XRF), ICP-MS, Adsorptive voltammetry (AV)	CRMs: TDB-1, UMT-1, SARM-7	(Zereini et al. 1997b)

(Part 1 of 3)

Table 2.7.1. (cont.) Methods for analysis and validation of Pd in soils and plants

Determined PGE	Sample Matrix	Sample Digestion Method	Separation /preconcentration	Instrumental technique	Method validation	Reference
Pd, Pt	Sewage sludge, Dust, Soil, Grass	Ashing in a muffle oven, Melting with sodium peroxide and HCl dissolution	On-line column preconcentration	GFAAS with flow injection system, ICP-MS, INAA, Electrothermal atomization laser atomic fluorescence spectrometry, Differential pulse cathodic stripping voltammetry (DP-CSV)	Recovery tests, CRM: SARM-7	(Helmers et al.1998)
Pd, Pt, Ru, Ir	Road dust, Surface soil samples	HPA, aqua regia, Microwave (MW) digestion, HF	Chromatographic separation by anion-exchange	ID-Q-ICP-MS	CRM: WGB-1 (Canmet); Interlaboratory study	(Müller and Heumann 2000)
Pd, Pt, Rh	Soils	HCl	NiS fire assay	INAA		(Heinrich et al. 1996)
Pd, Pt	Plants	Ignition, acidic acid, magnesium nitrate, HCl, $KMnO_4$	Extraction with MIBK+ benzene	GFAAS	Recovery tests	(Kothny 1987)

(Part 2 of 3)

Table 2.7.1. (cont.) Methods for analysis and validation of Pd in soils and plants

Determined PGE	Sample Matrix	Sample Digestion Method	Separation /preconcentration	Instrumental technique	Method validation	Reference
Pd, Pt, Rh	Tobacco, Beans		On-line extraction preconcentration system	GFAAS, Inductively coupled plasma atomic emission spectrometry (ICP-AES)	Standard addition method	(Lee et al. 1993)
Pd, Pt, Rh, Ru, Os, Ir	Soils	HPA, HCl, HNO_3, MW-digestion	Cation-exchange chromatography	ID-ICP-MS	CRMs: BCR-723 (road dust), WGB-1 (gabbro) and TDB-1 (basalt)	(Fritsche and Meisel 2004)
Pd, Pt, Rh	Soils, Plants	HPA, HCl, HNO_3, HF	NiS fire assay Te-coprecipitation using $SnCl_2$	ICP-MS	Independent method: GFAAS, Monitor-sample	(Schäfer et al. 1998)

(Part 3 of 3)

2.7.2 Experimental

Samples

- SARM-7 (Platinum ore, SA Bureau of Standards, Pretoria, SA) (Korotev 1996);
- JSd-2 (Stream Sediment, Geological Survey of Japan, Geochemical References Samples, Tsukuba, Ibaraki, Japan) (Imai et al. 1996);
- In –house standard road dust;
- Single element standard solutions Merk, CertiPure;
- Plant samples.

Digestion procedures

Procedure A: 0.1-0.2 g of the sample are treated with *aqua regia*. The mixture is left for 10 min and 2 mL aqua regia are added again. 10 min later 1 mL 48% HF is added and MW digestion is performed by Microwave MLS 1200 mega (MLS GmbH, Leutkirch, Germany), using the program, shown in (Djingova et al. 2003a). Afterwards 1.5 mL HCl are added twice and subsequent evaporation of the sample to incipient dryness is done. The residue is dissolved in 1.5 mL 0.5 M HCl and diluted to 50 mL.

Procedure B: 0.1-0.2 g of the sample are treated with 0.5 mL 37% HCl and 4 mL 65% HNO_3 and the sample is treated in HPA (max temp. 280 ^{o}C, max pressure 120b) for 160 min. The residue is subsequently treated with addition of 1 mL 48% HF and MW digestion. Afterwards sample evaporation on a sand bath is performed. Then 1.5 mL HCl are added twice and sample evaporation to incipient dryness and final dissolution of the residue in 1.5 mL 0.5M HCl are carried out. The final sample is diluted to 50 mL with bidistilled water.

Procedure C: 0.2-0.25 g of the sample are treated with 4 mL 65% HNO_3, 2.5 mL 37% HCl and 1 mL 48% HF and MW digestion is applied. Afterwards 5 mL saturated solution of H_3BO_3 are added and MW digestion is used again. The final sample is diluted to 50 mL with bidistilled water.

Procedure D: 0.1-0.2 g of the sample are treated with 3 mL 37% HCl and 0.5 mL 65% HNO_3 in PolyTetraFluoroEthylene (PTFE) vessels and left for 15 min. Afterwards 1.5 mL 48% HF are added to the mixture and MW digestion is performed. The procedure is repeated and is followed by evaporation of the solution on a sand bath. The residue is dissolved in 1 mL mixture of 2.5 % HCl and 1.3 % HNO_3. The solution is diluted to 50 mL with bidistilled water in naglene flasks and is measured immediately.

Plant material is completely digested using PTFE pressure vessels, mixture of 37% HCl and 65% HNO_3 and MW oven assisted system following the procedure described in (Djingova et al. 2003a).

All the reagents, used in the sample digestion and separation/pre-concentration procedures are of grade suprapure Merck (Darmstadt, Germany) and diethyl-dithiocarbamate (DDTC) is p.a. product of Sigma, Sigma-Alrdich, Dorset UK.

Separation/Pre-concentration of Pd

Extraction procedure

Separation of Pd from the interfering matrix elements is carried out by extraction of its diethyldithiocarbamate complex according the following procedure: The digested sample is treated with 0.5 mL 1 % KI for 5 min and pH is adjusted to 4 and kept with acetate buffer. 1 mL 1% diethyldithiocarbamate is added and extraction with chloroform is performed for 2 min. The extraction is repeated and the organic phases are united. (HPLC measurement is performed.)

The extract is evaporated to incipient dryness and the residue is dissolved in 1 mL 2.5% HCl and 1.3% HNO_3. After dilution immediate measurement by ICP-MS is done.

Ion-exchange procedure

Ion-exchange separation and concentration of Pd (together with Pt) is carried out using anion-exchange resin Dowex 1X10. Both elements are retained on the column as anionic chloro complexes and eluted by circulating thiourea at 60 ^{o}C, as described in details in (Kovacheva and Djingova 2002).

Instrumental techniques

ICP-MS

The measurements are carried out using a quadrupole ICP-MS spectrometer Perkin-Elmer Sciex ELAN 6000 with cross flow nebulizer. The measurement conditions, used in the analysis, are presented in (Djingova et al. 2003a).

ICP-AES

Comparative measurements are carried out using ICP-AES analysis – Spectroflame D (Spektro Analytical Instruments, Kleve, Germany) with Meinhard concentric glass nebulizer. The used operating parameters are shown in (Kovacheva and Djingova 2002).

Table 2.7.2. Results from the analysis of SARM-7 after four digestion procedures

	A	B	C	D	Certified value
Pd [mg/kg]	1.25± 0.08	1.38± 0.10	1.28 ± 0.10	1.51 ± 0.16	1.53 ± 0.30
Recovery [%]	82 ± 5	90 ± 6	84 ± 6	99 ± 4	

HPLC

The measurements are performed at 297 nm using UV detector, C_{18} 10µm stainless steel column (Deerfield, IL) with dimensions 250x4.6 mm and mobile phase acetonitrile-water (70:30). The flow rate is 1.6 mL/min.

2.7.3 Results

Digestion

The investigation of the four digestion procedures described in the experimental part has been carried out initially using SARM –7. Table 2.7.2 presents the results obtained by ICP-MS measurement and the respective recoveries. Each result is a mean value of 8 replicates and the standard deviations are presented as well.

Although there is not a substantial difference between the recoveries and all results are very reproducible further procedure D has been applied in the case of analysis of soils, sediments, street dust and geological materials.

Separation and preconcentration procedures

In our laboratory two separation/preconcentration procedures have been developed. The first one is based on ion-exchange (Kovacheva and Djingova 2002) and the second one – on extraction (Djingova et al. 2003). Both procedures may be used depending on the subsequent measurement technique.

Table 2.7.3 presents the results from the validation of the procedures. The results are obtained from analysis of model solutions, SARM-7 and JSd 2.

Table 2.7.3. Results from the determination of Pd after ion-exchange and extraction [ng/g]

Sample	Certified value	Ion-exchange	DDTC extraction
Standard solution	5	4.82± 0.03	4.93±0.05
JSd 2	21.2	21.6± 1.2	21.0±0.6
In-house standard street dust	100	95±8	93 ± 6
SARM-7	1530	1500±30	1497 ±25

Measurement techniques

Three analytical techniques have been used for measurement of Pd in the investigated samples. Initially investigations with model solutions were carried out to evaluate qualitatively and quantitatively the interferences for each technique in the analysis of soils, sediments and plants. For this purpose single element and mixed solutions in the concentration range 5 – 100 ng/mL for Pd and 10 – 100 µg/mL for the interfering elements were used. Table 2.7.4 presents the potential and the established interfering elements for the three techniques. In the case of ICP-MS the established interference is presented as relative % from the concentration of the interfering element in brackets after the respective element. For HPLC the experimentally established peaks of the potentially interfering DDTC complexes under the experimental conditions are also given in brackets.

Verification of ICP-MS measurement using the proposed method (separation of Pd as DDTC complex)

To validate finally the ICP-MS method for determination of Pd in various environmental materials analysis has been performed of SARM-7 (1530 ng/g), JSd-2 (21.1 ng/g), in-house road dust material (100 ng/g) and a mixed element solution (600 ng/g). The dependence between measured and certified concentrations is presented in Fig. 2.7.1. Further on in the analysis of samples these CRMs and model solution were used for calibration of the spectrometer thus covering a wide range of matrices and concentrations. Of course each time the CRMs and element solution are subjected to the whole procedure and the linearity of the curve is checked. Such approach (calibration of the spectrometer with various CRMs with increasing concentration and different matrices has been already successfully used in our laboratory

Table 2.7.4. Interferences in the instrumental determination of Pd by ICP-MS, ICP-AES and HPLC

ICP-MS		ICP-AES		HPLC as DDTC complex
^{105}Pd	$^{40}Ar^{65}Cu^+$, $^{35}Cl_3^+$, $^{89}Y^{16}O^+$ (4.6% Y) $^{88}Sr^{16}O^1H^+$ (0.063% Sr)	Pd (I) 340.458 nm	Zr	Co (5.92min), Cu (7.78 min) Ni (5.46 min) Cr Hg, Pb, Zn
^{106}Pd	^{106} Cd (0.056%Cd), $^{40}Ar^{66}Zn^+$, $^{90}Zr^{16}O^+$, (2.4%Zr) $^{89}Y^{16}O^1H^+$, (0.7%Y)	Pd (I) 363.47nm	Ce, Th, Zr	
^{108}Pd	^{108} Cd^+, $^{40}Ar^{68}Zn^+$, $^{92}Zr^{16}O^+$(0.83%Zr) $^{92}Mo^{16}O^+$ (0.08%Mo)			

for XRF analysis of samples with strongly varying composition (Kuleff et al. 1999).

Verification of ICP-AES measurement using the proposed method (ion-exchange separation of Pd)

Similar approach (calibration with CRMs, in-house standard and single element solutions) was used for the verification of the ICP-AES procedure developed at the laboratory. The linearity is checked in the concentration range 20 – 2000 ng. ($R^2 = 0.9976$).

Cross validation of ICP-MS and ICP-AES

Road dust, sediment and a plant sample have been analyzed by both ICP-techniques and the results are demonstrated in Fig. 2.7.2 indicating the very good agreement of the results. The detection limits of the methods are 0.02 ng/g for ICP-MS and 15 ng/g for ICP-AES. Thus the determination of Pd in plants by ICP-AES is possible only in single cases when the concentration exceeds this limit.

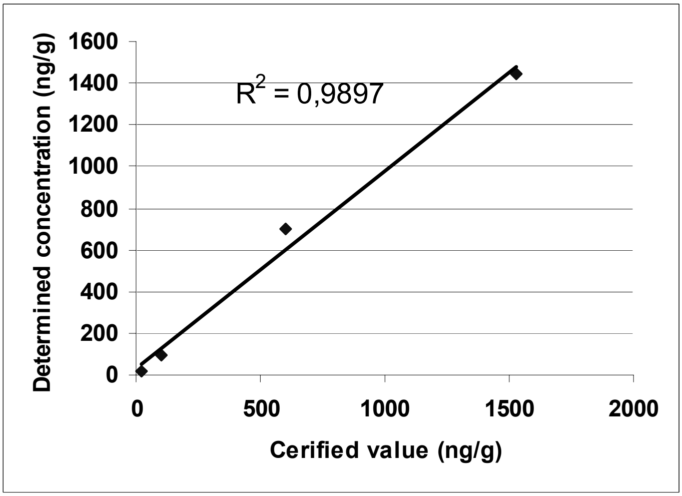

Fig. 2.7.1. Dependence measured/certified concentration for Pd by ICP-MS using SARM-7, JSd-2, in-house road dust and element solutions

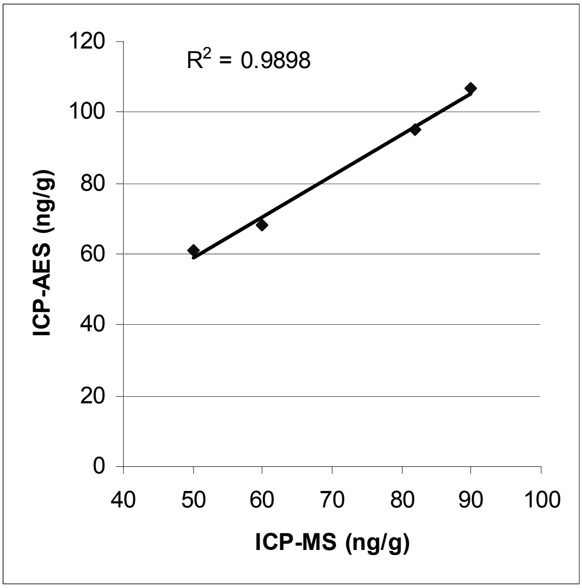

Fig. 2.7.2. Comparison of results for Pd by ICP-MS and ICP-AES

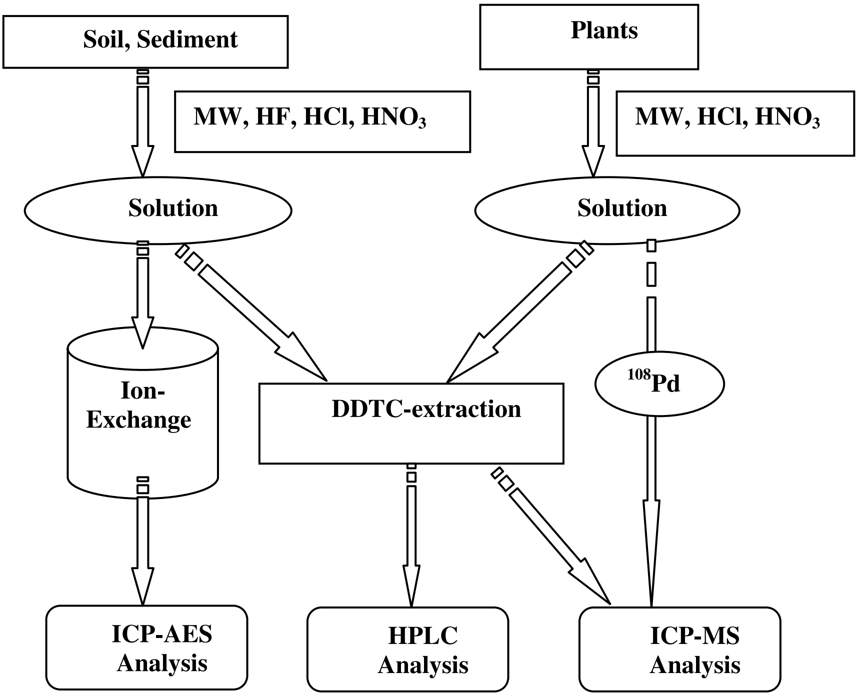

Fig. 2.7.3. Analytical validation scheme using ICP-MS, ICP-AES and HPLC

2.7.4 Discussion

Method validation studies rely on determination of overall method performance parameters. These are usually obtained during method development, interlaboratory study or following in-house validation protocol. Validation demands verification of each analytical step, identification of potentially significant influence factors, and determination of one or all of the following parameters: linearity, precision, accuracy, detection limit, selectivity, robustness or ruggedness.

The aim in our laboratory has been to develop independent methods for determination of Pd in environmental materials using various digestion, preconcentration procedures and measurements techniques and thus to compensate for the lack of appropriate standard reference materials and to perform quality control.

Fig. 2.7.3 presents the scheme used for the validation of the methods developed for Pd determination. Some of the steps undertaken in this direction are discussed below:

Digestion

All the three techniques under consideration work with digested samples, therefore the digestion step is of utmost importance especially when a variety of samples with different matrices are to be analyzed, the CRMs are quite different from the samples and the analyte (in this case Pd) most probably is in different forms in the investigated materials. Thus it is necessary to ensure complete digestion of the investigated materials either by investigating of CRM or by comparison of different digestion procedures.

In the literature different procedures for complete sample digestion are described (see Table 2.7.1). The complete wet acid digestion of silica containing materials (soils, dust, ores and sediments) requires the presence of hydrofluoric acid, accompanying different acid mixtures (mainly combinations of HCl, HNO_3 and $HClO_4$). The addition of boric acid to the sample at the end of the digestion assures the transformation of the hydrofluoric acid into tetrafluoroborates and thus makes the system compatible to further separation/pre-concentration procedures (Boch et al. 2002). There is evidence (Godlewska-Żyłkiewicz 2004), that the widely used mixture of HF and $HClO_4$ for complete digestion of samples should be avoided when subsequent ion-exchange separation of PGEs is carried out, due to a risk of considerable losses. HPA is a compulsory step in the digestion procedure for organic matter decomposition when cathodic stripping voltammetry (CSV) analysis is performed (Zereini et al. 1997b, Gómez et al. 2002, Zereini et al. 2004,). It is also used to improve the leaching of PGE from different kinds of matrices (Balcezak 2002). MW digestion is a quite efficient and preferable sample treatment for complete matrix decomposition. It is successfully used to improve the total digestion both of silica and no silica containing matrixes (e.g., Müller and Heumann 2000, Boch et al. 2002, Gómez et al. 2002).

For investigation of this step in our experiments initially SARM-7 was chosen because on the one hand it was the only available CRM where direct measurement of Pd by ICP-MS is possible (high concentration of Pd and PGM and relatively low concentration of interfering elements) so that only the digestion step could be evaluated. On the other hand SARM-7 has a very complicated and difficult matrix for digestion and might be used for conclusions for easier matrices as soils and sediments. Three MW digestion procedures (A, C, D in Experimental part) have been used with various ratios of the acids and different ways of discarding the remaining HF. Procedure D has been accepted for digestion of all sediments, soils and geological samples. It is worth mentioning that after the methods have been developed it was proven that all 4 procedure provided complete leaching of

PGE for road dust samples. The comparison between results from digestion of plant samples using procedure D and the procedure described in the experimental part for plants gave no statistically significant difference.

Separation and preconcentration procedures

Different procedures for chemical pretreatment, including separation and concentration of PGEs from the sample are elaborated and specific improvements at different stages of the analysis are performed in order to overcome the existing analytical problems and to achieve the necessary quality assurance. A detailed review, considering the different procedures for separation and pre-concentration of Pt and Pd for spectrochemical determination is published by Godlewska-Żyłkiewicz (2004). Ion-exchange, liquid-liquid and solid phase extraction, co-precipitation and electrochemical pre-concentration remain the most frequently used procedures for sample pre-treatment for determination of Pd and other PGE in the environment (see Table 2.7.1). Some of them are currently improved and directly connected to the instrumental technique (e.g., Lee et al. 1993, Boch et al. 2002, Godlewska-Żyłkiewicz and Zaleska 2002, Matusiewicz and Lesiski 2002, Fan et al. 2004, Fritsche and Meisel 2004,).

In our studies we have chosen ion-exchange (Kovacheva and Djingova, 2002) and DDTC extraction (Djingova et al. 2003a) as methods for separation and concentration of Pd. Both procedures are characterized with high and reproducible yields. Ion-exchange is better suited for use before ICP-MS and ICP-AES measurements while DDTC extraction is intended for HPLC but may be used with any of the other two techniques. After the complete digestion of the samples no specific effects form the matrix have been established in any case. The throughput for the ion-exchange procedure is 3-4 samples per hour while for the extraction procedure it is 7-8 samples pro hour.

Measurements techniques

After separation and preconcentration of Pd by the above procedures any of the three measurement techniques might be used. In the case of ICP-MS and ICP-AES there are no interfering elements present in the solution. For HPLC however all the diethyldithiocarbamates of the transition metals might be present. Therefore the instrumental conditions should be controlled and optimizes each time.

Under these experimental conditions ICP-MS is to be recommended having the lowest detection limit. The other two techniques have similar detection limit (15-20 ng/g). However in case the concentrations of Pd in the investigated material are above the detection limits of both techniques, ICP-AES is preferable due to the lack of interfering elements in the sample solution. At present in our laboratory HPLC is used as an independent method for the verification of the formation of Pd-DDTC.

2.7.5 Conclusion

The validation of a method is a rather time consuming and expensive process especially when the methodology is rather new, there are no appropriate CRM, and no direct methods for comparison as in the case of Pd. The present paper demonstrates an approach for validation by using several CRMs, single and mixed element solutions for calibration, two separation methods and three measurement techniques. An approach for calibration of the spectrometers with different CRMs and mixed element solutions (after performing the separation and preconcentration steps) is proposed as a way to overcome the problem with the lack of appropriate reference materials.

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2.8 ICP-MS and Te Co-Precipitation after Nickel Sulphide Fire-Assay Collection for Pd Determination in Roadside Soils

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2.8.1 Introduction

The analytical determination of palladium derived from car emissions and deposited on topsoil has close resemblance to the determination of palladium in geological samples in general. On Earth's crust Pd occurs associated with other precious metals (Pt, Rh, Ir, Ru and Os, which are collectively known as platinum group elements, PGE). Their abundance is very low (just few ppb or even less) and mineralised rocks may contain just few parts per million of PGE, as discrete platinum-group minerals and in solid solution in sulfides, arsenides and sulfarsenides (Cabri 1992). Palladium is also sometimes found associated with gold (Cabral *et al.* 2002). The random and inhomogeneous distribution of PGEs phases implies that when precious metals are to be determined in rock, sediment and soil samples, large sample mass should be taken (at least 5 g, but it can be as large as 50 g, Potts 1992). The commonest analytical techniques require that sample should be taken in solution, to separate the precious metals from the matrix elements and an easy choice could be acid dissolution. Among the precious elements used in catalytic converters, palladium has the larger mobility (Wood and Middlesworth 2004), which is associated to the higher solubility of this element, which was attributed to reactions with nitrogen oxides (Amossé and Delbos 2002).

As in minerals, in catalytic converters Pd is alloyed with other precious elements and total dissolution requires strong oxidizing reagents, like *aqua regia*. The solubility of PGE containing phases in *aqua regia* is substantial, but not always complete (Gowing and Potts 1991) and it can be quantitative if pressure is applied, in apparatus like Carius tubes or a high pressure asher (Pearson and Woodland 2000, Pennebaker and Denton 2001, Meisel *et al.*

2003, Fritsche and Meisel 2004). The use of closed vessels has constrains regarding sample mass and alternatives are fusion methods. One successful procedure is the sintering or fusion with sodium peroxide (Enzweiler et al. 1995; Morcelli and Figueiredo 2000) which has been successfully applied to large samples mass (Amossé 1998; Amossé and Delbos 2002).

Another fusion method is the so-called fire assay (also known as docimasy or FA). In this method, a large sample is fused in alkaline fluxes (usually mixtures of sodium carbonate and sodium tetraborate) and metallic compounds which will collect precious metals. The most frequent collectors are lead (added to the initial sample+flux as lead oxide or carbonate) or nickel sulphide (added as metallic Ni and elemental S). Lead is used for Au collection and Pd can be also quantitatively recovered. When other PGEs are of interest, nickel and sulphur are used (NiS). This is also the choice when analysis of PGE associated with catalytic converters deposited on soils is of interest. During sample fusion, the nickel sulphide phases separate from the slag, sinking to the bottom of the clay crucible and the small droplets coalesce, forming a button which size depends on the initial amounts of Ni and S. Precious metals are collected by the NiS, due to their high affinity (partition coefficient) to the sulphide phase. The coprecipitation with Te after the HCl digestion of the NiS button is reported to improve the PGE recovery (Shazali *et al.* 1987).

Here we describe the analytical method of NiS-FA and Te coprecipitation followed by ICP-MS as applied to the determination of Pd originated from catalytic converters in roadside soils collected from a high traffic road in São Paulo, Brazil. Method accuracy was evaluated by the analysis of geological reference materials with Pd certified values.

2.8.2 Experimental

NiS Fire Assay with Te co-precipitation:

Organic matter was removed by calcining soil samples in an oven furnace, heated first at 200°C for 2 hours and subsequently at 650°C for 4 hours. NiS buttons were prepared after thoroughly mixing 10-15 g of sample and the fusion mixture, which consisted of 10 g of sodium carbonate (anhydrous extra pure, Merck), 20 g of sodium tetraborate (anhydrous GR, Merck), 1 g of nickel powder (INCO Metals) and 0.75 g of purified sulfur (Merck). The mixture was transferred into a fire clay crucible and fused at 950 °C for 30 minutes, and for another 30 minutes at 1050 °C. After cooling, the crucible was broken, the NiS button was retrieved from the slag, crushed into large particles and weighed. The NiS button was dissolved with 20 mL of Suprapur® hydrochloric acid (Merck) in a Teflon closed vessel (Savillex, USA), at 150 °C on a hot plate for about 14 h. The resulting solution was cooled to room temperature, diluted with 5 mL of deionized water (Milli-Q, Millipore) and of 2 mL of a 2000 μg g^{-1} Te solution, prepared as described by Stockman (1983), were added. The solution was heated to 95-100°C and 10 mL of a Sn(II) chloride solution (13.5 g of $SnCl_2.2H_2O$ dissolved in 9 mL of concentrated HCl and diluted to 60 mL with water), freshly prepared, were slowly added to precipitate the metallic Te. The solution was boiled to coagulate the precipitate, 1 mL of the Te solution was added, and the solution was boiled for 5 minutes. The tellurium solution was added twice in order to improve the PGE collection in the precipitate, as described by Oguri *et al.* (1999). This solution was then filtered onto a 0.45 μm membrane filter (Millipore) and the precipitate was washed with a 10% v/v HCl solution. The membrane was firmly grasped by its rim with the aid of small tweezers, and inclined into a Teflon vessel. A mixture of 2 mL of HCl and 2 mL of Suprapur® HNO_3 was carefully dropped on the precipitate, which was dissolved and diluted with 10 mL water. The solution was transferred to a polypropylene flask with the aid of a funnel and made up to 50,00 g with water for ICP-MS analyses.

HR-ICP-MS

A HR-ICP-MS Instrument, Element, Finnigan MAT, was used. The instrumental parameters and the isotopes used are described in Table 2.8.1. Palladium method detection limit (3σ) obtained for procedural blanks, in three replicate measurements of two different blanks, was 0.1 ng g^{-1}. The HR-ICP-MS Instrument was calibrated with solutions containing 0.2; 0.4; 0.8; 1.0; 2.0; 5.0; 10.0 and 20.0 ng mL^{-1} of Pd prepared from a PGE standard solution (Specpure, ALFA AESAR). A 10 ng mL^{-1} indium solution was used to optimize the instrumental parameters and to maximize the signal intensity. Potential interferences from MO^+, MOH^+, and MAr^+ species were evaluated in previous works (Shibuya *et al.* 1998; Jorge *et al.* 1998) and none were found to be significant for the range of concentrations measured for this work.

Table 2.8.1. HR-ICP-MS (Element, Finnegan MAT) operating conditions and measurement parameters

Inductively coupled plasma	
Resolution	300
RF power	1350 W
Argon gas flow	
Sample gas	1.0 L min^{-1}
Auxiliary gas	0.92 L min^{-1}
Cooling gas	15 L min^{-1}
Data acquisition parameters	
Counting statistics	10x2 (runs and passes)
Sample uptake rate	1 mL min^{-1}
Skimmer and sampler cones	nickel
Measured isotope (isotopic abundance %)	^{103}Rh (100), ^{105}Pd (22.23), ^{193}Ir (62.7) and ^{195}Pt (33.8)

2.8.3 Results and Discussion

Reference Material Analysis

The precision and accuracy of the analytical method were assessed by the analysis of the reference materials WPR-1 (altered peridotite), UMT-1 (ultramafic ore tailings), TDB-1 (diabase rock), WGB-1 (gabbro rock), all from CANMET and GPt-3 (peridotite) and GPt-4 (pyroxene peridotite) from IGGE, China (Table 2.8.2). These reference materials were selected for the present study due the presence of PGE in ranges similar to those found in environmental samples and because there is no soil reference material with Pd certified value available.

Although the number of replicates was not enough to be representative, the results tend to be within the certified value and the uncertainty of two standard deviations (Kane 1991) for GPt-3 and GPt-4 reference samples. Results of the other four reference materials can be directly compared to the associated 95% confidence interval. Results of Pd in TDB-1 and WGB-1 fall within this confidence interval, while results of UMT-1 and WPR-1 are outside the interval, but still acceptable for the purposes of evaluating the distribution pattern of Pd emissions by from catalytic converters used in cars, with average relative errors close 10%. The reproducibility of the

Table 2.8.2. Pd concentrations in the certified reference materials (ng g^{-1})

RM	Obtained*	Certified value**
GPt-3	5.0 ± 0.7 (n=3)	4.6 ± 0.6 (*)
GPt-4	61 ± 17 (n=3)	60 ± 9 (*)
UMT-1	115 ± 13 (n=2)	106 ± 3
WPR-1	210 ± 44 (n=3)	235 ± 9
TDB-1	22.8 ± 2.0 (n=2)	22.4 ± 1.4
WGB-1	13.9 ± 2.5 (n=2)	13.9 ± 2.1

*= uncertainty represents ± one standard deviation of n replicates; ** = if not otherwise stated, ± represents 95% confidence interval

method, calculated as relative standard deviations, ranged between 9 and 28%, is comparable to the expected precision at the ng g^{-1} concentration level (Horwitz and Albert 1995). As a whole, the analytical procedure can be considered reliable for the determination of Pd in analyzed matrices.

In spite of the great number of studies concerning the PGE determination by NiS-FA, especially in rock and mineralized samples, there are still some points, not yet well understood, which interfere in the recovery of Pd and PGE in general. Considering the very low concentration of PGE expected in environmental samples, care must be taken in the analytical procedure to obtain reliable results.

First of all, let us make some considerations about the recovery of the PGE in the NiS fire assay. Several authors have studied the relationship between the collector amounts, the charge (sample + flux) and the S to Ni mass ratio. Robert *et al.* (1971) suggested a flux to sample ratio of 1:1, and 20 g of NiO and 10 g of S for 90 g of flux. Parry *et al.*(1988) and Jackson *et al.* (1990) reported the use of 10 g and 5 g of Ni as the collector. Asif and Parry (1989) reported that 0.5 g of Ni was effective for PGE recovery for high level samples. Paukert and Rubeska (1993) concluded that minimizing the mass of the NiS button does not influence the recovery of PGE. Low recoveries of the PGE using NiS collection are reported in the literature (Jackson *et al.* 1990). Frimpong *et al.* (1995) studied the problems in the recovery of PGE using NiS-FA at nanogram per gram concentrations. These authors observed that the recoveries of Ru, Rh, Pd and Pt in a komatiite sample which contained <10 ng g^{-1} of PGE were reproducible and varied systematically with collector masses. The partition coefficient ($Kd = [PGE]_{sulfide}/[PGE]_{silicate}$) obtained for the a komatiite sample was up to 103-fold lower than for the PGE ore sample (SARM-7), showing that analytically significant amounts of Ru, Rh, Pd and Pt fractionated into the silicate phase and were not recovered by the NiS, using a 1g Ni collector. In this work, it was observed, in the analysis of WPR-1, that a ratio of S/ flux+sample > 5% increased about 10-15% the recovery of PGE. In many procedures, NiS buttons are crushed or pulverized before treatment with acid, but some authors report losses of PGE during this operation (Boisvert *et al.* 1991). In this work, better results were obtained when the NiS button was crushed into large particles instead of pulverizing the button.

The problems of interferences in ICP-MS also need to be taken in account. We verified that the interferences of $^{88}Sr^{17}O$, $^{87}Sr^{18}O$ $^{87}Rb^{18}O$ in the analysis of ^{105}Pd were less than 0.01%. The interference of $^{35}Cl_3^+$ polyatomic ion was observed on ^{105}Pd and corrected. According to previous experience of the authors in the analysis of PGE by ICP-MS (Jorge *et al.* 1998, Figueiredo *et al.* 2000), it may be considered that the problems of interferences in ICP-MS were not responsible for the errors observed in the results.

Zischka and Wegscheider (2000) estimated overall standard uncertainties of about 10-30% for the determination of Au, Pd, Pt and Rh either by *aqua regia* leaching or Ni-docimasy as sample preparation techniques followed by ICP-MS, depending on the analyte and the combined analytical method used. Isotopic dilution, which consists in spiking the sample with enriched isotopes of the elements of interest during the first stages of sample preparation has been used in some studies (Meisel *et al.*, 2003; Fritsche and Meisel, 2004; Rauch *et al.* 2004). This accurate internal calibration technique does not require quantitative recovery, but for isotopic equilibration full solubility of elements of interest is necessary. It also cannot be applied to monoisotopic elements (eg. Rh) and isobaric and polyatomic interferences still need to be corrected.

Roadside Soil Analysis

Roadside soils from a major road (SP348), in São Paulo, Brazil, with high traffic flow (ca. 30000 vehicles/day), were analyzed. Sampling points were between the cities of São Paulo and Jundiaí, where there is the highest density of traffic of the road, at 31, 39, 45 and 55 km from São Paulo. Areas of

20 m^2, forming a rectangular grid, were sampled. Composite samples were then prepared by taking 5 samples, collected at each 1 m, along a 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. The sampling depth was 5 cm. The results obtained were described elsewhere (Morcelli *et al.* 2005).

In order to illustrate the considerations about the use of ICP-MS and Te co-precipitation after nickel sulphide fire-assay collection for Pd determination in roadside soils, we present, in Fig. XX.1, the results obtained**,** where Pd concentration in the continental crust is also presented (Morcelli *et al.* 2005). This value was used as reference since no information is available about PGE levels in Brazilian soils.

The Pd concentration ranged from 58 to 1.1 mg kg^{-1}. The highest concentration obtained is more than two orders of magnitude higher than geogenic background value for Pd. At about 140 cm of the roadway the concentrations are ca. 90% lower compared to the samples collected at 40 cm from the road, which indicates the anthropogenic origin of Pd. These data agree with results obtained in other studies, where higher concentrations of the PGE were also observed in the vicinity of roadways (Schafer & Puchelt 1998; Morton et al. 2001). The catalyst converters used in Brazil are mainly composed by Pd and Rh and the data here presented are the first Pd values obtained for Brazilian soils, considering the car emissions inputs.

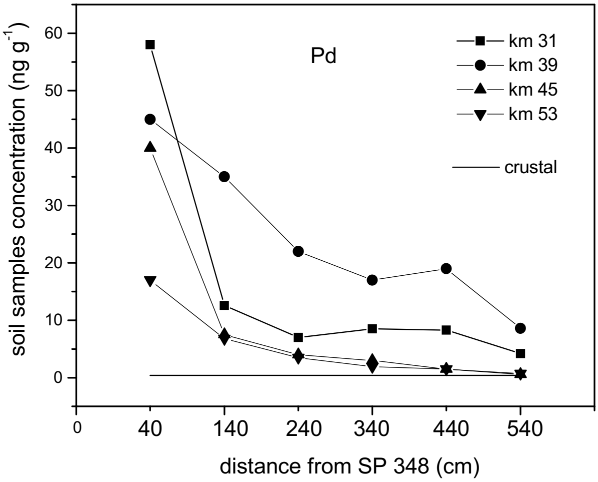

Fig. 2.8.1. Distribution patterns of Pd in roadside soil samples collected at SP348

2.8.4 Conclusions

The use of NiS fire assay with co-precipitation of Te and HR-ICP-MS is a powerful tool to determine Pd in different geological matrixes. The results obtained for Pd analysis in different reference materials showed the reliability of the method. It was applied to soil samples because of the similarities between the matrices and because Pd emissions of catalytic converters present some common characteristics with Pd occurrences in rocks, like uneven distribution and occurrence as metallic particles. This approach is of great importance in view of the lack of proper certified reference materials for environmental samples. The results obtained for the roadside soils evidenced the adequateness of the analytic method. The absence of at least one certified soil reference material could mean that the absolute values of Pd in the analyzed roadside samples may be a little different. However, in this case, the absolute values are less important, and the significant differences found in Pd concentration in relation to the distance of the road are relevant enough to characterize the catalytic converter origin of Pd.

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2.9 Determination of Ultra-Trace Levels of Palladium in Environmental Samples by Graphite Furnace Atomic Spectrometry Techniques

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2.9.1 Introduction

Palladium, one of the platinum group elements (PGEs), has received an increasing attention during the past 15 years by manufacturers of automotive catalytic converters (ACCs) (Johnson Matthey, 2004). Pd-rich ACC units exhibit a more efficient elimination of harmful and/or toxic components of exhaust gases (e.g., CO, NO_x, and hydrocarbons) originating from diesel- and petrol-fuelled vehicles and some household utensils. Moreover, due to the advantage of Pd catalysts at lower working temperatures, they are successful in decreasing the level of exhaust fumes at cold starts of engines. Thus, cars equipped with these novel ACC units can meet even stricter emission limits for petrol-fuelled vehicles. On the other hand, the concentration of anthropogenically evolved PGEs, including Pd, has been continuously increasing in the environment since the introduction of ACCs (Zereini and Alt, 2000; Ravindra et al., 2004).

Anthropogenic Pd has been reported to be mobile and bio-accumulated by aquatic organisms, generally, to a larger extent than Pt and Rh (Sures et al., 2001, 2002a; 2002b). Moreover, metallic Pd has an allergenic potential on humans (Van Ketel and Niebber, 1981). Therefore, the monitoring of the level of Pd in various environmental compartments and biological matrices appears to be an important task in order to assess the risk of this element to human health and the environment.

Graphite furnace atomic absorption spectrometry (GFAAS) is a selective, and sensitive analytical technique, thus, it has been widely applied to the determination of Pd in a large variety of environmental/biological matrices (Bencs et al., 2003). In environmental compartments and biological matrices, however, the concentrations of PGEs are fairly low (pg g^{-1} – ng g^{-1} level), which often requires the application of pre-concentration/

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matrix separation steps prior to their GFAAS detection (Bencs et al., 2003; Godlewska-Żyłkiewicz, 2004). The low level of Pd is also true for almost all the matrices exposed to a major anthropogenic emission source of PGEs, e.g., heavy traffic sites (Zereini and Alt, 2000; Ravindra et al., 2004).

Electrothermal vaporization (ETV) sample introduction methods comprise the vaporization of samples from a graphite/metal sample holder inserted within a resistance heated graphite furnace and subsequent transport of the evolved sample vapours to the detection source. Therefore, ETV studies also supply with very important data on the vaporization behaviour of analytes/matrices, and thus the literature generally refers to ETV as a complementary technique to GFAAS. This consideration is also a motivation for incorporating the ETV-related studies on Pd together with GFAAS into the present study.

2.9.2 Methods of sample preparation

Storage of samples

Sampling procedures, the handling of samples and the dissolution/digestion procedures have an ample influence on the accuracy and precision of analytical methods used for the determination of Pd at the ultra-trace level. Special pre-caution is required for the purification of decomposition agents and vessels employed to achieve appropriately low blank levels (Godlewska-Żyłkiewicz, 2002). The proper choice of vessels for the storage of samples has been verified in the case of Pd, as hydrolysis/adsorption arises for weak acidic conditions on long standing. Sorption losses of Pd^{II} up to 90 % were observed in three weeks, when utilizing polyethylene or polyethylene-polypropylene vessels for storage. On the other hand, the sorption loss was found to be negligible from quartz containers (Matusiewicz and Lesinski, 2002). Moreover, quartz vessels are advantageous for opening up samples and, additionally, they also provide better storage properties and lower blank values, particularly after thiourea plus HCl cleaning pre-treatment (Godlewska-Żyłkiewicz, 2002). A detailed assessment on the impact of storage material and the solution chemistry of Pd can be found in a recent review (Godlewska-Żyłkiewicz, 2004).

Digestion methods

A number of methods have been offered for digestion of Pd-containing environmental matrices, such as acidic dissolution, fusion methods, the application of chlorination and fire assay (i.e., fusion and collection of Pd on a metal sulphide, - usually NiS - button, also referred to as "docimasy") procedures (Zereini et al., 1994; Urban et al., 1995; Heinrich et al., 1996; Zischka and Wegscheider, 2000).

Zereini et al. (1994) studied the alternative utilisation of lithium and sodium tetraborates as flux constituents in fire-assay procedures prior to GFAAS determination of PGEs in standard reference materials (e.g. SARM-7). Lithium tetraborate had a lower recovery compared to that of sodium tetraborate, except the chromitite ores with PGE contents in the ppm range. For chromitites, the optimal condition was proved to be the use of a 1:1 mixture of these borate salts. Electronprobe microanalysis (EPMA) revealed a finer grain-size of the PGE phases with the use of lithium tetraborate, and a coarser with sodium tetraborate. The finer grain-size could be the reason for the greater analyte losses during filtration. Urban et al. (1995) investigated the composition of a variety of phases formed on NiS-buttons by EPMA. They observed diverse PGE-containing phases, according to the varying flux constituents and PGE species added. They have found considerable losses of PGEs during the analytical steps following the fire-assay, when their levels in the sulphidic-phases were high, which is more likely to be dissolved. Thus, special attention should be paid to the determination of Pd by NiS fire-assay methods.

The most regular decomposition method is the acidic dissolution, based on the application of aqua regia plus hydrofluoric acid (HF), the latter applied only in the presence of silicate matrix constituents. Microwave (MW) ovens, high-pressure PTFE bombs and high-pressure ashers (HPAs) are used to decompose a variety of matrices; e.g. road dust, soil, airborne particulate, and biological materials. Accurate analytical results were also obtained without the application of HF for "difficult" silicate-containing matrices (e.g., road dust) particularly via *aqua regia* leaching under high-pressure and -temperature conditions (Müller and Heumann, 2000). Despite this, in some cases, Pd has been reported to be strongly bound to silicate matrices compared to other PGEs, which demands efficient HF digestion procedures (Limbeck et al., 2003). Vaporization of the excess HF can be avoided by addition of boric acid (Boch et al., 2002). For biological materials, such as blood samples, mineralization or decomposition by UV photolysis is generally recommended before nebulization of the sample solutions (Begerow et al., 1997a), whereas urine can be measured directly by GFAAS, i.e., without decomposition of the samples (Begerow et al., 1997b). An overview of the decomposition methods is included in Table 2.9.1.

Table 2.9.1. Analytical methods for the determination of Pd in various environmental/biological samples

Matrix	Digestion /dissolution method	Pre-concentration /separation	Technique	Calibration technique	LOD (ng l^{-1}, if not indicated otherwise)	Reference
Car exhaust fume	- (Solid sampling on graphite plates with an Anderson-type cascade impactor)	-	ETV-Q-ICP-MS (direct insertion of the graphite plates with samples)	Calibration constant determined from standards	-	Lüdke et al., 1996
Human urine	-	Extraction of pyrrolydine dithiocarbamate complexes with 4-methyl-2-pentanone	GFAAS	Matrix matching	20	Begerow et al., 1997b
Airborne particulate	Leaching with H_2O_2 and HNO_3 in MW oven	Electrodeposition/ adsorptive accumulation on pyro graphite tube	GFAAS	Standard addition	Electro depos.: 60 (= approx. adsor. accum.)	Komárek et al., 1999
Road dust	H_2O_2 and HNO_3 in MW oven (+HF addition)	FIAS (N,N-diethyl-N'-benzoyl-thiourea complex on C_{18})	GFAAS	Against simple standards	18	Boch et al., 2002
Beans, tobacco	HNO_3 + HCl with HPA digestion	CMDTC on XAD-4 resin,	GFAAS	Standard additon	30	Lee et al., 1993

Table 2.9.1. (cont.) Analytical methods for the determination of Pd in various environmental/biological samples

		or liquid-liquid extraction with dithizone				
Human hair and urine	$HNO_3 + H_2O_2$ with MW	Cloud point extraction with *O*,*O*-diethyl-dithiophosphate and Triton X-114	ETV-Q-ICP-MS	Std. solutions subjected to the same pre-concentration as the samples	6.0	Da Silva et al., 2001
Urban aerosols, road dust	HNO_3 in closed PTFE vessel, opened and $HF+HClO_4$ addition	FIAS (with DEBT complexing agent on C_{18} micro column)	GFAAS	Acidic standards	23	Limbeck et al., 2003
Road dust	$HNO_3 + HCl +$ HF, in HPA	Electrodeposition on glassy carbon, or graphite electrode in a flow-through cell	GFAAS	Acidic standards	50	Godlewska-Żyłkiewicz and Zaleska, 2002
Road dust, soil, plant	Pyrolysis at 400 ^{o}C, aqua regia digestion	Dithizone fixed on Diaion resin	GFAAS	Standards were prepared the way as samples	0.2 (ng g^{-1})	Chwastowska et al., 2004
Zebra mussel	MW digestion conc. HNO_3	-	GFAAS	Standard addition	90 (ng g^{-1})	Zimmermann et al., 2003
Road dust, rock, anodic slime, ACC	Aqua regia digestion	Adsorption of dimethylglyoxime complex on silica gel	GFAAS	Acidic standards	400	Tokalioğlu et al., 2004

Note: Q-ICP-MS - quadrupole ICP-MS; FIAS - flow injection analysis system

General considerations on electrothermal vaporization

ETV sample introduction methods incorporate the vaporization of samples from a graphite/metal sample holder by resistance heating and subsequent transport of the evolved vapours to the detection source. For detection purposes, inductively coupled plasma mass spectrometry (ICP-MS), and inductively coupled plasma atomic emission spectrometry (ICP-AES) techniques are most frequently applied. As it is known from the literature, ICP-MS methods are hampered by severe mass spectral interferences during the determination of PGEs, including Pd, which arise from the presence of argon plasma gas, sample matrix, and dissolution agents (Zischka and Wegscheider, 2000; Bencs et al, 2003). The means to overcome these interference effects include application of solid sample introduction devices: e.g., ETV unit to produce dry aerosols. This technique is also one of the so-called *Thermal Sample Introduction* (TSI) methods (Kántor, 2001). The basic concepts of ETV sample introduction techniques were discussed in detail by Kántor (1988).

Studies on palladium with ETV techniques

In the earliest report, Grégoire (1988) examined the feasibility of ETV for the introduction of PGEs to the ICP-MS. The home-made ETV device contained an electrothermally heated, pyrolytically coated graphite strip for the deposition and vaporization of the samples. An argon stream was introduced tangentially to the metal supports of the graphite strip, whereas a quartz cover was placed above the vaporization surface to minimise condensation of the sample vapours (i.e., losses), thus maximizing the aerosol transport to the plasma. PGEs behave as refractory elements in the graphite furnace. Therefore, a fast heating ramp and the application of the maximum permissible vaporization temperature (*ca.* 3000 K for graphite furnaces) were recommended to record fast transient signals with maximum peak height. The matrix effect of Ni originating from the fire assay digestion step was also examined. Using ETV, a 500 ppm Ni matrix increased the signal of Pd by around 4-10-fold; these enhancement effects were utilized to increase the detection power of the method.

Byrne et al. (1997) studied the vaporization and atomization of all the six PGEs utilizing an ETV-ICP-MS tandem technique. A very similar vaporization mechanism was concluded for five PGEs (Pd, Pt, Ir, Rh, and Ru), which includes, as a first step, the conversion of the PGE salt to metal in the ETV unit, and then the vaporization of this metallic form. This mechanism was independent of the presence of simple matrices such as HNO_3, HCl, and $TeCl_2$. It is to be noted here that in the regular methodology of the ETV technique, vaporization temperatures greater than 2000 ^{o}C are required for a complete vaporization of PGEs.

Lüdke et al. (1996) mounted graphite plates into an Anderson-type cascade impactor to collect diverse size-fractions of particles (between 0.35 and 16.5 μm cut-off diameter) originating from car exhaust fumes. The graphite plate, containing the sample, was subsequently inserted into an ETV unit for the simultaneous ICP-MS determination of Pd, Rh, Pt and Ir. When the sampled volume contained small amounts of particles, during the analysis of the impaction target "discrete" signals originating from single particles were detected. In this case, based on Poisson-statistics, one can calculate the number of particles from the relative standard deviation of the signal. Moreover, the mass of each analyte per particle can be calculated with the aid of a calibration constant. The concentrations of the element pairs for both Pt-Rh and Pd-Ir revealed good correlation with the PGE content of ACCs used for the period prior to sampling. It was deduced that Pt and Rh originated from the abrasion of ACC material. On the other hand, Pt showed a poor correlation with both Pd and Ir, indicating that the latter two elements were from other anthropogenic sources.

Da Silva et al. (2001) applied a cloud-point extraction procedure based on the complexation of Pd with *O*,*O*-diethyl-dithiophosphate (DDTP) and subsequent extraction of Triton X-114 (non-ionic surfactant). This separation technique involves the increase of the temperature up to the cloud point, where a phase separation occurs. The surfactant-rich phase contains most of the complexed analytes and, since the surfactant volume can be very small, high enrichment factors generally result. The organic phase was subjected to ETV-ICP-MS determination. DDTP was also found to be a thermal stabilizer and physical carrier of analyte atoms. The optimal pyrolysis and vaporization temperatures for Pd are found to be around 1200 and 2500 ^{o}C, respectively.

For the separation of Pd from biological and environmental matrices, low-volatility diethyldithiocarbamate complexes of Pd were produced and vaporized in an ETV unit at a fairly low temperature (1100 ^{o}C) by Fan et al. (2004). The measurement conditions, which affect the formation and vaporization behaviour of Pd-chelates, were found to be the ashing temperature and time, the vaporization temperature and time, pH, and chelate concentration in the sample solution. Similar to this approach, the chelating resin of YPA_4 (aminoisopropylmercaptane-type resin with polythioether support) was also utilized for the pre-concentration of Pd and its low temperature (1900 ^{o}C) vaporization in an ETV unit (Wu et al., 2004a). After complexation of the analyte, the slurry was prepared from the resin, which could be directly introduced into the ETV device. The advantage of this method is that it makes possible an "in-situ" separation of Pd from Pt, based on the diverse vaporization characteristics of their YPA_4 complexes (Wu et al., 2004b).

ETV sample introduction has definite advantages over conventional, nebulization-based sample introduction methods used for liquid/slurry samples: (1) higher sensitivity; (2) tolerance for the analysis of samples with high acid and organic matrix content; (3) less probability of interferences in the detection source achieved via selective vaporization of the analyte/ matrix constituents; (4) facility to analyse small sample volumes (some µl), and (5) ability to directly analyse solid samples without any laborsome sample pre-treatment step.

On the other hand, ETV methods have certain shortcomings originating from graphite material used as vaporization surface; i.e., carbide formation, deterioration and memory effects, which are manifested as delayed and/or tailed transient peaks. When a metal ETV is used, the durability (fairly short life-time) and the reduced temperature range appear to be limitations (McLeod et al., 1992). The matrix-dependent volatility of analytes in ETVs can be overcome by proper choice of heating programs or addition of volatilisation agents (e.g., Freon, PTFE powder) to the samples, the latter being very suitable for the evaporation of refractory elements (Kántor, 2001). For solid sample introduction ETV methods, the sample amount inserted into the vaporiser unit is restricted to 10 mg or less. Moreover, the homogenisation of samples by micro-pulverization and sieving is often a requirement, which diminish one benefit of direct solid sampling, i.e., the minimal sample preparation (McLeod et al., 1992).

2.9.3 GFAAS techniques

General

In GFAAS analysis, typically a 20-100 µl volume of the sample solution, or 0.1-1.0 mg of solid sample is dispensed into a graphite atomizer mounted in the optical path of a spectrometer. As a first step of the measurement cycle, the sample is pre-treated (dried, and pyrolyzed) in an attempt to remove the matrix constituents, and then atomised with electrothermal heating to produce free atomic vapour of the analyte. Graphite furnace atomizers provide nearly a 100- to 1000-fold increase in the residence time of the sample vapours in the optical path compared to flame and ICP excitation-atomization sources. Certainly, a lower dilution of the sample vapour is also true for the analyte, as well as for the matrix constituents, which give rise to greater gas-phase (chemical) interferences (Kántor, 2001). Additionally, the accessible calibration range is usually lower than required to cover the concentration values usually occurring in environmental/biological samples. Although GFAAS is generally referred to as a single element technique, the most up-to-date instruments possess simultaneous, multi-element capability for up to six analytes (Radziuk et al., 1995a; 1995b).

Direct, solution-based GFAAS determination methods

The GFAAS determination of PGEs, as can be deduced from ETV studies noted above, requires high atomization temperatures due to the high vaporization temperature of the PGE compounds. It is to be noted here that for small sample amounts, i.e., below the µg mass-range, the vaporization of the sample constituents takes place around their melting points rather than their boiling points. Several matrix constituents, especially chloride salts of transition metals, have been reported to cause interference effects with GFAAS measurements (Welz and Sperling, 1999).

Early-developed GFAAS methods for Pd determination in plants and biological materials are based on peak height data evaluation. The tube geometry, heating rate, the type of acid, and its concentration have been reported to significantly affect the magnitude of the Pd signal (Farago and Parsons, 1982). Line selection was also found to be important to keep the noise as low as possible, i.e., the selection of the analytical line of Pd 340.46 nm was found to be more suitable for samples with high background (e.g. plants) than the more sensitive, but noisy Pd 247.64 nm line.

Most of these problems can be overcome by the usage of the most robust, commercially available GFAAS instruments, which offer the possibilities for stabilized temperature platform furnace (STPF) conditions (Slavin et al., 1981) and Zeeman-effect background correction in connection with a transversely heated graphite atomizer (THGA). GFAAS systems, based on the STPF concept, provide higher and more homogeneous temperature conditions in the atom reservoir for the vaporization/atomization of PGEs, and a less intensive extent of chemical and/or physical interferences. These conditions result in some two orders of magnitude linearity of the calibration curves, which is a necessary compromise for solving the analytical problems using instrumentation with lower maintenance costs as compared to ICP-MS.

Overcompensation by the background corrector during the determination of Pd was observed in the presence of Pb, as the Pb 247.64 nm line affects the Pd 247.642 nm line. To overcome this interference, either the Pd 244.79

nm, or the Pd 276.3 nm line could be selected, and/or the pyrolysis temperature could be increased to 1200 ^{o}C to remove the interfering matrix constituent (Brzezicka and Szmyd, 1999).

It is to be noted here that the chemicals involved in the pre-concentration/separation procedures for Pd could also interfere with its GFAAS determination. For example, KSCN complexing agent was found to cast a high non-specific absorption on the AAS signals of Pd; this shortcoming did not appear for glycine and thiourea (Godlewska-Żyłkiewicz et al., 2000). Moreover, at 1.2 mol l^{-1} concentration, thiourea increased the Pd signal by some 10 %.

Matrix separation and pre-concentration methods

As was aforementioned, the quantitation of the ultra-trace levels of PGEs in environmental/biological samples requires pre-concentration of the analytes, and/or separation of the matrix for their detection by GFAAS. For instance, Patel et al. (2000) used Sn^{II} chloride and N-butylacetamide as complexing agents for the separation and enrichment of Pd from soil samples. This method was based on the formation of Pd(II)-$SnCl_3^-$-N-acetamide and the liquid-liquid extraction of this complex with 1-pentanol, followed by the GFAAS measurement.

Godlewska-Żyłkiewicz et al. (2000) applied a Cellex-T resin for the pre-concentration and GFAAS determination of Pd and Pt in tap water and in catalytic converters. Glycine, thiourea and KSCN were utilized as suitable complexing agents for the elution of Pt and Pd from the microcolumn. Glycine was found to be the most successful agent for the separation of Pt and Pd, since it forms complexes of different charges with these elements.

Fully automated on-line pre-concentration of Pd was accomplished on a micro-column loaded with the strong complex forming agent N,N-diethyl-N'-benzoylthiourea (DEBT) (Schuster and Schwarzer, 1996; 1998). The Pd complex was eluted with 60 µl ethanol and directly transferred to the graphite platform for GFAAS determination. From a 45 ml sample solution, a 1200-fold sensitivity enhancement was achieved, with a LOD of 3 ng l^{-1}. In 6.5% (v/v) HNO_3 solutions, alkaline, alkaline-earth, and transition metal ions, such as Cd^{II}, Co^{II}, Cu^{II}, Fe^{III}, Ni^{II} and Zn^{II}, were tolerated up to 10 g l^{-1}, or higher concentrations. The authors found coupling with the GFAAS method more rugged than those with laser excited atomic fluorescence spectrometry (LEAFS), or ICP-MS. Although the latter techniques result in a lower LOD, they necessitate more expenditure of work and modification of the pre-concentration method (Schuster et al., 2000). A similar coupled GFAAS method was applied to the determination of Pd in road dust (Boch et al., 2002; Limbeck et al., 2003) and urban aerosol samples (Limbeck et al., 2003; 2004). In these studies, the DEBT complexing agent was also applied for pre-concentration purposes to bind Pd on a C_{18} micro-column.

Lee et al. (1993) elaborated on-line pre-concentration of Pt, Pd and Rh as bis(carboxymethyl)-dithiocarbamate (CMDTC) complexes on an XAD-4 filled microcolumn after the off-line addition of solid CMDTC to the sample solution containing $SnCl_2$ and HCl. The sample solution was segmented in the pre-concentration unit by air in order to prevent dispersion. The eluate was collected on-line in a PTFE loop and was forced either into the graphite furnace by nitrogen, or into the ICP by the use of a carrier solution. The pH of sample solutions, the concentration of the complexing and reducing agents, and the flow rate in the column were also studied and optimised.

Begerow et al. (1997b) applied the pyrrolidinedithiocarbamate complex forming agent for the determination of physiological levels of Pd from urine sample (pH=4). The complexes were separated by liquid-liquid extraction into 4-methyl-2-pentanone (2 minutes is the minimum required extraction time to access the maximum extraction recovery), which resulted in a 25-fold enrichment. A polystyrene-based sorbent with DETA (cross-linked polystyrene with diethilenetriammine complex forming groups) was also efficiently utilized for the pre-concentration of all six PGEs (Kubrakova et al., 1996).

Chwastowska et al. (2004) used dithizone sorbent for a selective separation of Pd from road-dust, soil and plant samples. Either thiourea or nitric acid was used as an eluent for the removal of Pd from the complexing column. However, the large excess of thiourea is reported to evolve during the pyrolysis stage in the graphite furnace, producing corrosion of graphite tubes. The pyrolysis step also demands slow heating (100 s ramp) and a fairly high temperature (1200 ^{o}C) for the decomposition and complete removal of the thiourea matrix. It was also shown that the total amount of Pd introduced in various chemical forms (oxide, nitrate) into soils could be extracted by aqua regia.

Green algae (*Chlorella vulgaris*) immobilized on a Cellex-T support was also utilised for a selective binding of Pd (bio-sorption) at pH 1.5-1.8 from sample solutions of spiked tap- and waste-water, and natural grass (Dziwulska et al., 2004). Thiourea (0.3 mol l^{-1}) in 1.0 M HCl solution was proved to be the most effective stripping agent for Pd. The presence of interfering ions common in these matrices, such as Co^{II}, Cu^{II}, Fe^{III}, Mn^{II}, Na^{I}, Ni^{II} and Zn^{II}, was tolerated up to 0.1 g l^{-1}. The LOD of the method was 96 ng l^{-1}.

Komárek et al. (1999) proposed the adsorptive accumulation and electrodeposition of Pd and Pt onto the internal surface of a pyrolytically coated graphite tube, which subsequently served as an atomization surface for GFAAS measurements. For this purpose, a flow-through cell was used for introducing the sample solution into the graphite tube, for supporting the deposition of the sample aliquot into the middle part of the tube. The sample position is of significant importance for end-heated tubes which, compared to the side-heated designs, have an inhomogeneous temperature distribution along the longitudinal axis. Generally, for the former atomizers, the preferred atomization site is the middle of the furnace. This region can reach the nominal preset atomization temperature. The sensitivities, which depended on the flow-rate and sample volume applied in the ”deposition” cell, were essentially the same for the two different enrichment techniques: i.e., 8-24 times higher for Pd and Pt than with the standard deposition of 20 µl sample aliquots. Similar electrodeposition methods were employed for Pd in dust samples prior to GFAAS determination (Matusiewicz and Lesinski, 2002).

Pre-concentration of Pd from tap water and road dust samples on a graphite electrode was performed in a flow-through electrochemical cell at a controlled potential prior to their GFAAS measurement (Godlewska-Żyłkiewicz and Zaleska, 2002). After pre-concentration of Pd, the polarization of the electrodes was changed and the deposited metal was dissolved with the assistance of a proper stripping agent.

LEAFS equipped with GF-ETA vaporization/atomization source and also GFAAS were applied to the determination of Pd in airborne particulate matter (Tilch et al., 2000). The pre-concentration procedure was similar to that employed by Schuster and Schwarzer (1996). Using this enrichment technique combined with ETA and LEAFS detection, a very enhanced detection power was achieved with an LOD value as low as 2 ng l^{-1}, which was lower by approximately one order of magnitude than the corresponding value obtained by GFAAS.

2.9.4 Conclusions

Due to the intensifying anthropogenic emission of Pd, interest in its determination by both GFAAS and ETV-based tandem techniques has gained increasing attention. ETV coupled to a sensitive detection source (e.g. ICP-MS) and GFAAS with proper matrix separation/pre-concentration are very suitable methods for the quantification of Pd from materials often referred to as “difficult”, such as environmental and biological matrices. ETV sample introduction provides the possibility of selective vaporization of the matrix constituents and the analyte, thus it may be helpful in elimination of certain interferences occurring during the detection of Pd.

The complementary use of ETV tandem techniques and GFAAS methods is of certain importance in view of the lack of proper certified reference materials for most of the environmental compartments and biological systems exposed to Pd emission by ACCs. This consideration is valid for almost all of the matrices studied for the evaluation of the impact of anthropogenic Pd, which certainly demands forthcoming efforts from analytical chemists. In the future, due to the continuously increasing Pd levels in the environment, the application of less sensitive analytical techniques (such as direct, solution-based GFAAS) can become also a leading analytical approach in this particular field of analytical chemistry.

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2.10 Determination of palladium in road dust and sewage sludge ashes

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2.10.1 Introduction

The increasing industrial use of palladium in many fields of technology led in the recent years to wide investigations on its toxicological effects and emission in biosphere. Studies on noble metal contents in ancient ice clearly show lower amounts of palladium than in recent snow samples (Van de Velde et al. 2000) which can only be explained by its increasing use in the last decades. Even though many investigations were done on potential risks to palladium, yet no final assessment to the effect of this exposure can be given. Studies over the last 20 years show high allergenic potential of palladium especially in connection with dental alloys to patients and dental personal (Castelain and Castelain 1987, Augthun et al. 1990, Suhonen and Kanerva 2001, Vamnes et al. 2004). Other sources for general population to come into contact with palladium might be jewellery containing palladium and emissions from Pd automotive catalytic converters. Workers occupationally exposed to Pd include miners, dental technicians, road workman and chemical workers.

Looking at the world's palladium demand over the last 10 years, in 1999 a maximum of about 260 t was reached, thenceforward the demand went down to approx. 140 t in 2003. Itemizing the several applications for palladium its demand for auto catalyst industry is by far the highest one. Second highest demand shows dental application. (Product information Palladium 2004) Accepting these facts, especially those environmental compartments should be investigated for their palladium content that are directly or indirectly influenced by these two applications.

However, every environmental sample is a complex mixture of a variety of mostly unknown compounds and therefore determination of palladium in ultra trace range requires analytical methods with high selectivity and detection power. Highly sensitive methods, such as inductively coupled plasma mass spectrometry (ICP-MS) or instrumental neutron activation analysis (INAA) suffer from strong spectral interference (Köllensperger et al. 2000, Djingova et al. 2003, Schwarzer et al. 2000). Highly selective separation and enrichment techniques are the best way to overcome these problems. Examples for such systems are the recently developed system for the determination of Pd and Au based on co-precipitation of the previous metals with mercury and subsequent measurement by total-reflection x-ray fluorescence spectrometry (Messerschmidt et al. 2000) or the fully automated flow injection column pre-concentration system developed by Schuster and Schwarzer (1996, 1998) that can be coupled with many atomic spectroscopic methods. The latter system, coupled to graphite furnace atomic absorption spectrometry (GFAAS) was used to obtain the results of the present work, providing a detection limit of 18 ng Pd l^{-1} from a sample volume of 2.7 ml.

For sample pre-treatment a simple microwave assisted digestion method for environmental samples containing silicates, phosphates, and oxides was developed, which is suitable for ultra trace analysis of palladium by the above mentioned column pre-concentration and determination technique. Sample weights of about 100 to 500 mg can easily be decomposed in a three-step digestion procedure with several mineral acids and hydrofluoric acid as active reagents. The often applied vaporization of excess hydrofluoric acid is avoided by the addition of boric acid, which transforms hydrofluoric acid to tetrafluoroborate, making the system compatible with enrichment procedures based on silicon containing micro-columns (Boch et al. 2002).

2.10.2 Determination of palladium in road dust

The introduction of palladium in automotive catalytic converters in Europe took place in the early nineties of the last century. Various parts of the environment, e.g. air (Rauch et al. 2001, Tilch et al. 2000), soil (Zereini, et al. 1997), road dust (Schramel et al. 2000) or grass (Schäfer et al. 1998) were investigated since then and almost all samples show increasing concentrations of this metal. Among all these samples, the composition of dust along heavily traveled roads is directly influenced by automotive emissions and is therefore useful for the determination of the elemental release of automotive catalysts. In order to record a time-dependent development of the palladium content in road dust, several tunnel dust samples were taken from 1994 to 2001 and analyzed for their Pd content. Tunnel dust seems to be quiet useful for this purpose, as influences of atmospheric effects are reduced to a minimum.

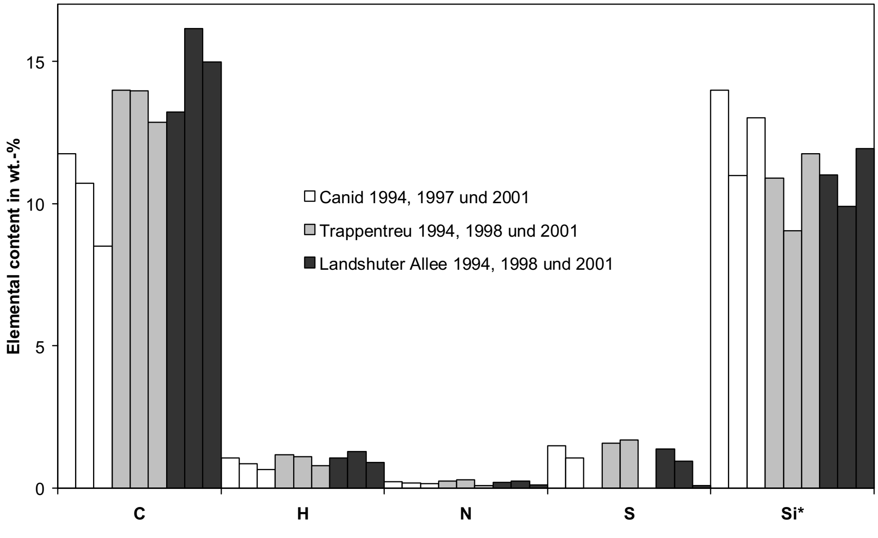
Table 2.10.1. Origin of the investigated Munich road dust and sampling dates

Origin	Date of Sampling		
Candid tunnel	August 1994	August 1997	February 2001
Trappentreu tunnel	August 1994	February 1998	February 2001
Landshuter Allee tunnel	August 1994	February 1998	February 2001

Sampling and matrix characterization

All samples (table 2.10.1) were taken from the roofs of emergency call boxes in Munich city tunnels “Candid”, “Trappentreu”, and “Landshuter Allee”. They were dried for 24 h at 120 °C and homogenized in a ball mill. Sieving of the material was not required, as only small dust particles settle on the roofs of the boxes.

Matrix characterization of the dust samples was performed by ultimate analysis for all samples and by total-reflection x-ray fluorescence spectrom-



* Silicon was determined by titration with molybdenum blue.

Fig. 2.10.1. C, H, N, S, and Si contents in Munich road dust

Table 2.10.2. Concentrations of elements in different Munich road dust samples of 2001 detected by TXRF

Element	Candid	Trappentreu	Landshuter Allee
	in wt.-%		
Ca	5,75	11,87	12,40
Fe	1,06	2,50	2,79
Zn	0,13	0,11	0,29
Ba	0,19	0,39	0,48
K	0,30	0,28	n.d.
Cl	0,12	0,20	0,10
	in mg kg^{-1}		
Cu	273	575	735
Mn	282	533	562
Sr	151	283	293
Cr	9	237	155
Pb	18	41	53
Ni	n.d.	59	58
As	7	28	21
Co*	2	4	4

n.d. not detected
* Cobalt was determined by GFAAS

etry (TXRF) for the samples of the year 2001. The results are given in fig. 2.10.1 and table 2.10.2.

As expected, the investigated dust samples do not differ significantly in their main constituents. The minor and trace constituents differ more, especially the Cr content of the sample Candid is comparatively low. Actually no explanation can be given for these variations as all sampling procedures were the same. For the optimization of the microwave assisted digestion especially the high Si and C contents, i.e. silicate and soot contents are important.

Sample digestion, measurement and recovery

Complete digestion of soot and silicate containing road dust requires the application of oxidizing reagents as well as hydrofluoric acid. To facilitate sample preparation, digestion was performed in a pressure and temperature controlled microwave digestion system (MULTIWAVE sample preparation system, Perkin-Elmer) in a three-step procedure (Boch et al. 2002). Digestion reagents were nitric acid, hydrogen peroxide and hydrofluoric acid. Boric acid was used for the masking of fluoride ions as tetrafluoroborate making the resulting solutions compatible with Pd enrichment on silicon containing micro-columns. Three independent digestions of each dust samples (sample weight about 100 mg) were performed and the resulting solutions were threefold measured by the on-line pre-concentration system coupled to GFAAS. Validation experiments resulted in a recovery rate of 98 ± 3 %.

Results and Discussion

The palladium contents of the dust samples are shown in fig. 2.10.2. The error bars drawn in the figure are single standard deviations, obtained by measurement of the three independent digestion solutions. For consideration, yearly Pd demand for European autocatalyst industry is marked in the figure (Product information Palladium 2004).

The palladium content of the three Munich dust samples has increased considerably from about 13.5-21.8 μg Pd kg^{-1} in 1994 to 138.2-281.6 μg Pd kg^{-1} in 2001. This dramatical rise in Pd content cannot simply be explained by the increase in traffic density (see Table 2.10.3), but it was most likely caused by an increase of cars equipped with palladium containing catalysts. This is in agreement with the values for the palladium demand of European autocatalyst industry drawn in fig. 2.10.2. Additionally, this assumption is supported by the rising platinum and rhodium content of tunnel dust samples (Helmers and Mergel 1998, Schäfer et al. 1999).

2.10.3 Determination of palladium in sewage sludge ashes

In sewage sludge ashes heavy metals of all urban emissions, also dental practice effluent, are enriched and so this matrix is suitable for the documentation of palladium emission caused by dental uses. Palladium based dental alloys were introduced in Western Europe in 1982 (Marx 1987), thenceforward an increase of palladium content in sewage sludge ashes is expected. In the same period of time, silver content in sewage sludge ashes

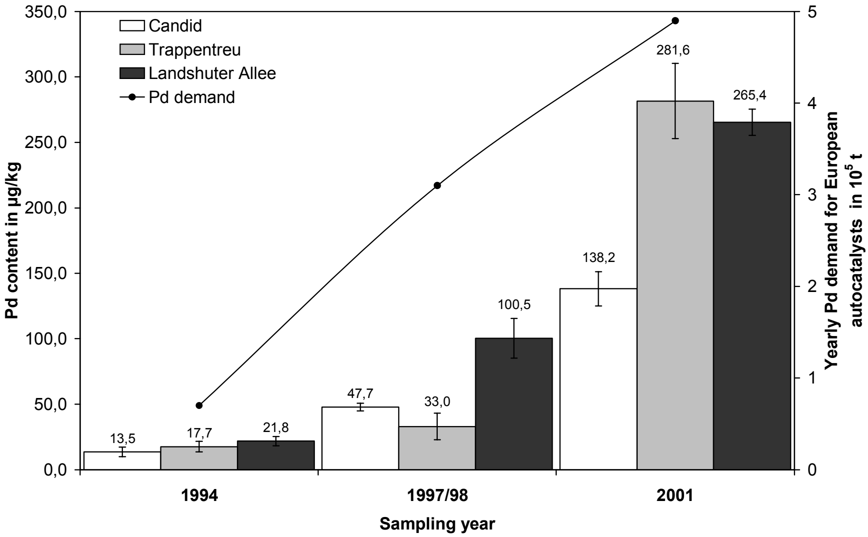


Fig. 2.10.2. Palladium contents of the road tunnel dust samples in µg Pd kg^{-1} and yearly palladium demand for European autocatalyst industry in 10^5 t

should decrease significantly in accordance to declining use of silver based dental alloys. As silver content in sewage sludge ashes is almost exclu-

Table 2.10.3. Traffic density of the Munich road tunnels in vehicles per day

	Year	Traffic Density [vehicles/day]
Candid tunnel	1994	n. d. a. *
	1997	ca. 94 000
Trappentreu tunnel	1994	ca. 110 000
	1998	ca. 126 000
Landshuter Allee	1994	ca. 100 000
	1998	ca. 118 000

n.d.a. no data available;
For the year 2001 traffic density was not measured

sively caused by dental uses, this correlation can be documented without influences (Hoppstock 1997).

Sampling and matrix characterization

The investigated sewage sludge ashes come from the main city sewage treatment plant Stuttgart-Muehlhausen, where resetting samples are archived since 1972. The average waste water inlet in this sewage treatment plant amounts to approximately 220 000 m^3 per day in case of dry-weather. After mechanical pre-clarifying, sludge digestion, and the biological treatment stage an amount of about 69 t sludge (dry weight) with a middle sludge age of 8-15 days results daily. This entire mass is nearly constant since 1972. The sludge is first drained by gravity thickener and centrifuged under employment of cationic organic reagents. After further thermal drying process water content is reduced to about 50% and the sludge is burned in a fluid bed incinerator at 950° C. As a result, daily about 35 t of ash are formed and separated by an electrostatic filter. Over the year, several ash samples are collected, consisting of random samples taken during a period of 10 days. The investigated ash samples are yearly mixed samples from these random samples. Their main components are listed in table 2.10.4.

Sample digestion, measurement and recovery

Since sewage sludge ash results from burning sewage sludge at 950°C organic components are already combusted and so the digestion procedure for subsequent element analysis must primarily dissolve the remaining inorganic matrix, i.e. silicates and sparingly soluble phosphates and sulphates. Therefore, the above described microwave assisted digestion proce-

Table 2.10.4. Main components of sewage sludge ash

Component	Content
Silicate	35 wt.-%
Calcium	13 wt.-%
Iron	10 wt.-%
Phosphate	7 wt.-%
Sulphate	3 wt.-%

(Data stated by the main analyses laboratory of the city sewage treatment plant Stuttgart-Mühlhausen).

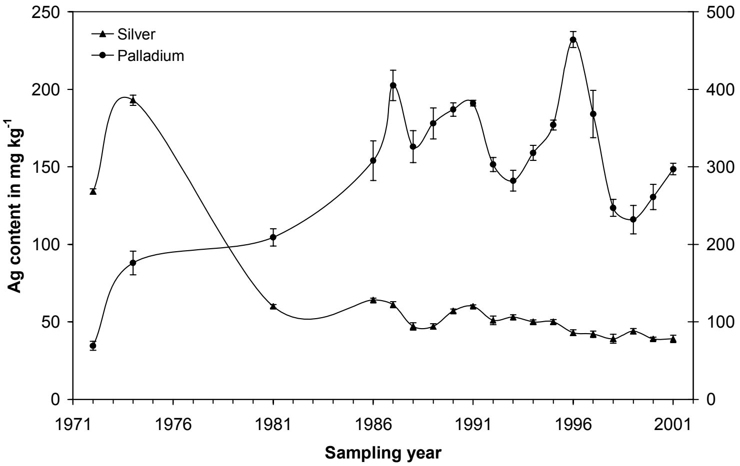


Fig. 2.10.3. Palladium and silver contents of sewage sludge ash samples from 1972 to 2001

dure must be adapted to this matrix. In addition to the digestion reagents used for the road dust samples, hydrochloric acid for the formation of soluble chlorocomplexes and sulphuric acid to dissolve sparingly soluble ferric phosphate are required. For each sample (100 mg) three independent digestions were performed and the resulting solutions were threefold analyzed for Pd by the on-line pre-concentration system coupled to GFAAS. Validation experiments resulted in a recovery rate of 105.7 ± 5.9 %. In addition, silver content of sewage sludge ash samples was determined by direct GFAAS analysis of the digestion solutions.

Results and Discussion

Palladium and silver contents of the investigated sewage sludge ash samples are presented in fig. 2.10.3. The error bars drawn in the figure are single standard deviations, obtained by the measurement of three independent digestion solutions. The measured silver contents tally quite well with values determined in sewage sludge ashes by Helmers and Wippler (1999).

The continuous discussion over the injurious character of amalgam fillings probably brought about a reduction of silver consumption in dental medicine. Application of alternative materials, among them palladium based dental alloys was enhanced. The expected correlation between the rise in Pd content in the ash samples and the decrease of Ag content on the

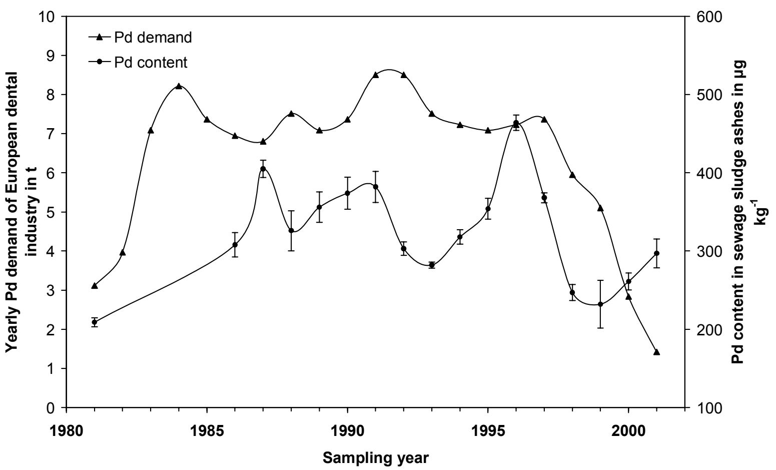


Fig. 2.10.4. Correlation of Pd contents in sewage sludge ash and Pd demand of European dental industry from 1981 to 2001

other hand is apparent (see Fig. 2.10.3). From 1974, when silver content reached a maximum with 193 mg kg^{-1}, it dropped within nearly fifteen years and found its level at about 40 mg kg^{-1}.

The obvious rise of the palladium content in sewage sludge ash took place before the introduction of the three-way automotive catalysts on palladium basis in Europe, which was in 1994. Therefore, it cannot be assigned to the discharge of Pd from automotive catalysts. However, there are further indications on the fact that a correlation exists between the sewage sludge ash composition and the intensified use of palladium in dental alloys. Fig. 2.10.4 illustrates the yearly Pd demand of European dental industry (Product information Palladium 2004) in comparison to the rise in Pd content in sewage sludge ash.

Annual palladium demand of European dental industry increased precipitously the first two years after the introduction of Pd based alloys in 1982. From 1984 to 1997 the demand varied between 7 and 8.5 t per year and dropped then to about 1.5 t in 2001. In comparison with this development the variation of the palladium content in sewage sludge ash is more unsteady, but besides those fluctuations it shows a similar trend. The obvious rise in Pd content of the samples from 1994 to 1996 might be influenced by the introduction of palladium auto catalysts in the European market.

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2.11 Speciation of Palladium in Plants: Method Development for Investigating Metabolic Changes

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2.11.1 Introduction

Since the introduction of noble metal based car catalysts in Europe, the three elements platinum, palladium, and rhodium have been a matter of concern in scientific and public discussions. Details about their respective emissions and fate in the environment are discussed in a monography (Zereini and Alt 2000). While in the beginning these discussions were focussing mainly on platinum, this changed in the 1990s due to the replacement of platinum-based car catalysts by palladium-based catalysts. In the meantime, the preferred active material for car catalysts (Pt or Pd) has changed to some extent from year to year, which is obviously due to the actual prices of the different noble metals on the world market. Therefore it is difficult to extrapolate a trend of catalyst based palladium emissions for the future, but it is already clear that the palladium concentration in the environment has increased considerably during the last decade (Schäfer et al. 1999, Palacios et al. 2000, Barbante et al. 2001). Moreover, it has been shown by several authors that the bioavailability of palladium to biota, i.e. plants (Schäfer et al. 1998) and animals (Artelt et al. 1999, Sures et al. 2001, Sures et al. 2002), is higher compared to that of platinum.

In order to understand the relatively high uptake rates and bioavailability of palladium, speciation methods are needed, which allow the separation and identification of the respective species in environmental samples and biomatrices. Unfortunately, up to now only very few publications on palladium species are available. For example, the complexation equilibria of model palladium(II) complexes with biologically important ligands like cysteine and glutathion (Bugarcic et al. 2004) or guanine and guanosine (Zhu et al. 2004) have been measured, the influence of oxalate and acetate on environmental palladium species has been calculated (Wood and van Middlesworth 2004), and for the chemotherapeutic lipoic-acid palladium complex (Antonawich et al. 2004) even bio-medical effects have been investigated in gerbils. But in the latter case no palladium species were directly analysed. The first results on the speciation of palladium in plant material have been published in the last three years (Alt et al. 2002, Weber et al. 2004, Lesniewska et al. 2004).

One reason for the lack of speciation methods for palladium lies in the fact that chemical analysis of palladium is even more difficult than that of platinum. Namely the use of the very sensitive ICP-MS is complicated by spectral interferences on all palladium isotopes. These interferences have to be removed by special sample preparation (Rauch et al. 2000, Hann et al. 2001, Bencs et al. 2003). Also adsorptive stripping voltammetry, which is successfully used for platinum (Hoppstock et al. 1989), is no alternative for palladium, because the detection limits are much higher. One solution to this problem was the introduction of a TXRF based method for reductive preconcentration and ultratrace determination of palladium (Messerschmidt et al. 2000), which allows a very selective determination of palladium with a detection limit in the low pg-range. This method was also the basis of the first investigations of palladium species in plants (Alt et al. 2002, Weber et al. 2004), which will be discussed in more detail in the following chapters.

2.11.2 Plant experiments and sample preparation

Plants are used for uptake experiments and biomonitoring, because they represent an important link between environmental pollution and metabolism in biota. Because of the very low palladium levels in ‘native’ (untreated) plants, speciation studies for this element have been done so far only with elevated palladium levels, i.e. after uptake of inorganic palladium to grass (Lesniewska et al. 2004) or lettuce (Alt et al. 2002, Weber et al. 2004). In Table 2.11.1, some parameters of these three investigations are summarised. More experimental details can be found in the respective references.

In all three cases, uptake of palladium was exclusively via the roots, and also the general sample processing (extraction, ultrafiltration and species separation by GPC or SEC) was quite similar - and comparable to that of previous platinum speciation studies of the same authors (Messerschmidt et al. 1994, Messerschmidt et al. 1995, Weber et al. 2000, Klueppel et al. 1998).

One interesting observation in the uptake studies of palladium in lettuce is that already after two days plants showed severe stress symptoms. Compared to platinum, these symptoms appear at much lower concentration, which limits the total amount of palladium that can be used for the experiments. This relatively low concentration of palladium imposes some prob-

Table 2.11.1. Investigations on uptake and speciation of palladium in plants

Plant species	Cichorium endivia	Lactuca sativa L.	Lolium multiflorum
Culture/time	Hydroponic/ 2 d	Soil / 14 d	Hydroponic / 8 d
Pd in nutrient solution	1 mg/L	4 mg/L	4 mg/L 40 mg/L
Pd in leaves	8,7 ng/g wet w.	10,3 ng/g wet w.	3,3 µg/g dry w. 8,3 µg/g dry w.
Pd-species	Proteins	Proteins	small molecules
extraction	Tris/HCl pH8	Tris/HCl pH8	Water, or Tris/acetate pH8
Ultrafiltration	10 kDa	10 kDa	10 kDa
Separation	GPC	GPC + ITP	SEC
Pd detection	TXRF	TXRF	ICP-MS
reference	Alt et al. 2000	Weber et al. 2004	Lesniewska et al. 2004

lems to the development of speciation methods; namely the number of consecutive separations, which can be applied without diluting the sample below the detection limit for palladium, is very limited.

This leads to two different strategies for obtaining information about palladium species: (i) using only one very rough separation, and measuring correlations of different detection channels, e.g. different elements by ICP-MS, (ii) developing a multi-dimensional semi-preparative separation scheme, which aims at the isolation and characterisation of distinct palladium species. These two strategies have been used already for the speciation of platinum in plants (Weber et al. 2000). For palladium, however, the concentrations are even lower, and also its chemical reactivity is higher. In other words: the risk of changing complex species equilibria by application of separation techniques is also higher. The relatively high stability of metalloproteins is the reason why the above mentioned strategy (ii) was applied first to high molecular mass proteins. For small Pd-species, strategy (i) was applied successfully to plants by coupling size exclusion chromatography to ICP-MS (Lesniewska et al. 2004), and for some of the separated Pd-species correlations are reported with co-eluting species of other elements (Ca, Cu, S). In the following paragraph, another correlation (Pd versus electrochemical detection) is emphasised as a way of detecting metabolic changes after uptake of palladium.

2.11.3 SEC separation of low-molecular-mass species and metabolic profiling by using electrochemical detection

Chromatographic separations, which make use of a size-based mechanism (size exclusion chromatography SEC, gel permeation chromatography GPC) are very popular as a first step to get an overview of metal species, which are present in a biological matrix. Although the chromatographic resolution is generally not very good, there is the possibility to gain at least some information about the size distribution of species, which then can be used for further separations. Moreover, SEC or GPC can be used in (semi-) preparative mode, and no extreme pH values or solvents are needed, which minimizes the risk of species changes.

In Fig. 2.11.1 the SEC separation of the low-molecular-mass fraction (< 10 kDa) of a grass root extract is shown with (a) the Pd distribution as measured by ICP-MS, (b) the pulsed amperometric detection (PAD) of a sample which was grown in Pd-free solution, and (c) the PAD detection of the

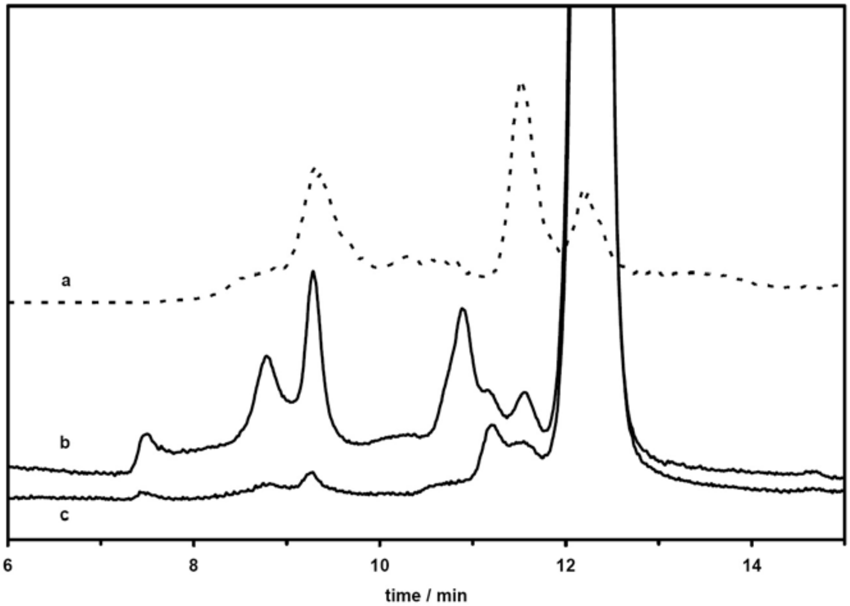

Fig. 2.11.1. SEC of small Pd-species in aqueous grass extract. $\mathrm{TSK_{gel}}$ G2500 column, 10 mmol/L NaCl at 0,75 mL/min, a: $^{108}\mathrm{Pd}$ (ICP-MS), b and c: PAD (detection potential +0,1 V vs. Ag/AgCl, cleaning at +0,6 V, regeneration at -0,8 V)

respective sample grown in Pd-containing nutrient solution. PAD is an electrochemical detection technique, which is selective especially for carbohydrates and related compounds.

Correlations of such compounds (as measured by PAD) have been reported already for platinum (Alt et al. 1998, Weber et al. 1998). Interestingly, it can be seen from Fig. 2.11.1, that the PAD-chromatogram for untreated grass (b) differs from that of Pd-treated grass mainly by a decrease in all relevant peaks, which contain Pd; with the exception of the largest peak at aroud 13 minutes. In the latter case it is impossible to see a change, because of the high concentration of the respective compound(s). It should be noted that the electrochemical detection is very reproducible, and the differences are statistically significant.

The decrease of PAD-detectable compounds (correlating with the appearance of Pd peaks) could be explained by one of the following hypotheses:

- Pd binds to such PAD-detectable compounds and thus inhibits their electrochemical detection (the compounds are still there, but are not detected)
- Uptake of Pd to the plant changes the metabolic pathways of such compounds, leading to smaller amounts of such species (in this case the decrease would be directly related to a decrease in the concentration)
- Uptake of Pd to the plant changes the metabolic pathways in such a way, that some of the detectable groups in carbohydrates are already oxidised (the compounds are still there, but their redox activity is changed)

At present, it is not possible to decide which explanation is correct. This is mainly because of the lability/reactivity of small Pd-species which make it very difficult to isolate single fractions for further spectroscopic identification. However, it seems that the electrochemical detection is well-suited to serve as an indicator for metal-uptake related metabolic changes. This is in agreement with the well-known suitability of electrochemical detection for metabolic profiling, e.g. for biomedical problems (Kaddurah-Daouk et al. 2004).

The identification of the small Pd-species correlating to electroactive compounds was not yet possible. The molecular masses of the respective retention window (~ 8-14 minutes, see Fig. 2.11.1) are in the range of about 100-400 Da, as estimated from the calibration of the SEC-column with amino acids and small peptides.

It should be noted that the chromatogram shown in Fig. 2.11.1 is not the full chromatogram; one more Pd-containing peak appears at about 20 min, which is due to inorganic Pd. It could reflect either the natural content of inorganic species, or it may have been formed as an artefact during separation (this cannot be fully excluded at the moment).

2.11.4 Combination of GPC and ITP for separation of high-molecular-mass species

For high-molecular-mass compounds (i.e. proteins) the risk of species dissociation is relatively low, and preparative scale gel chromatographic separations are often used for such metal species.

In Fig. 2.11.2 the GPC separation of a Pd-treated plant extract (lettuce) is shown (taken from Weber et al. (2004), with permission). In this first separation stage there is already a nice separation of 5-6 main peaks, but of course these ‘peaks’ do not reflect single substances, but a broad range of proteins. The respective molecular weights range from about 20 kDa to 1000 kDa.The appearance of several peaks in this molecular weight range upon treatment with noble metals has already been observed for platinum (Messerschmidt et al. 1994, Messerschmidt et al. 1995). Of course, the MW assignments only give a very rough estimation of the respective sizes of species, and it must be noted that this assignment may be problematic for two well-known but inevitable reasons: (i) the calibration of the column, which in this case has been done with globular proteins, may not reflect the behaviour of Pd-proteins (are they globular ?), (ii) one ‘peak’ in the figure is generally the sum of a mixture of several proteins, and by using the logarithmic scale calibration of GPC, even small changes in peak maximum correspond to quite big changes in molecular mass. Therefore, the only way to overcome these difficulties and uncertainties is to improve this rough separation by combination with other separation methods. For this purpose, methods based on a completely different separation mechanism are preferred. One such technique is isotachophoresis (ITP), and some typical results for using ITP as a second separation step after GPC are also shown in the lower part of Fig. 2.11.2. As an electrophoretic technique, the separation of ITP is based on the electrophoretic mobility μ_e, which is proportional to the ratio of charge q and radius r of an analyte. This means that bigger molecules will elute later than small molecules - provided the charge is the same. This is the reversed order compared to GPC, where larger molecules are eluted earlier than small ones. This reversal of elution order is indicated by the arrows in Fig. 2.11.2, showing that the Pd-species of GPC-fraction F2 elute later in ITP (350-450 min) than those of GPC-fraction F3 (250-350 min). Moreover, it can be seen, that ITP as a second separation step enables further separation of GPC fractions, resulting in about 5-7 separated peaks from one big GPC-peak.

The Pd amounts, which have to be detected in these ITP-fractions are already in the low ng- and even sub-ng-range. In Table 2.11.2, the absolute amounts of Pd, which are present in the selected peaks a-f (see Fig. 2.11.2)

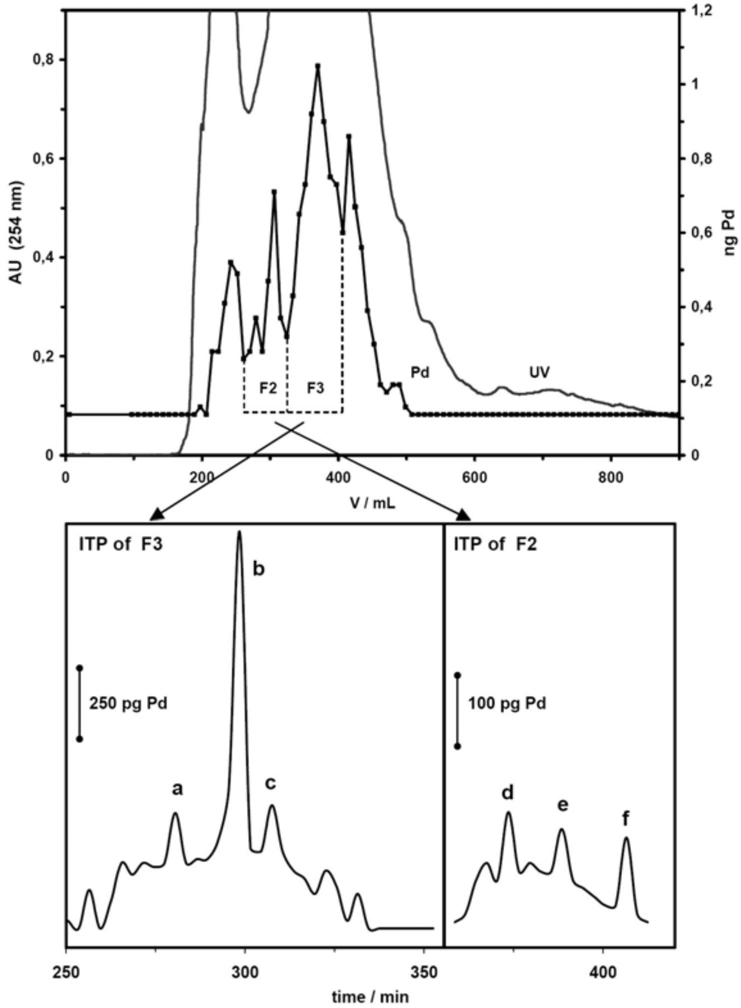

Fig. 2.11.2. GPC of Pd-protein-species in lettuce and further separation of two selected fractions by ITP. Pd determination by TXRF. GPC: Sephacryl S400, 20 mmol/L Tris/HCl pH 8 at 13,8 mL/h; ITP: Bio-Rad model 491 Prep Cell, leading electrolyte: 0,05 mol/L HCl at pH 8 (Tris), terminating electrolyte: 0,153 mol/L 6-aminocaproic acid at pH 8,9 (Tris), current: 8,5 mA (voltage 400-250 V). a-f: selected peaks (see text) (taken from Weber at al. (2004), with permission)

are given together with the respective molecular masses, which have been determined after isolation of the species and calibration using a HPSEC

Table 2.11.2. Total palladium amount in isolated species a-f, as shown in Fig. 2.11.2, and corresponding molecular masses

Peak (see Fig. 2.11.2)	a	b	c	d	e	f
Pd [ng]	1,08	3,10	1,46	0,40	0,46	0,30
MW [kDa]	69	89	106	120	150	200

column (Biosep-SEC-S4000, Phenomenex). This calibration of the isolated peaks is more reliable than the estimation using the rough GPC separation. Moreover, the isolated peaks can be further separated by using ITP. But, as expected, the results confirms that these peaks are not single proteins, but still consist of several substances. Unfortunately, it is impossible to quantify Pd after this third separation step; the respective amount would be in the low pg- and partly in the sub-pg-range, which is below the detection limit of the TXRF procedure for Pd, which is about 20-30 pg Pd.

2.11.5 Conclusions and Outlook

Until now, there are only very few data available on the speciation of palladium in plants, and it is not clear if the published results are typical for all plants, all experimental settings, etc. (most probably they are not). However, some conclusions can already be drawn with respect to analytical demands, biological relevance, and future needs:

First of all, there is a need for improvements in trace analytical methods for palladium. Speciation of palladium in plants is really a very challenging task, due to the low concentrations and the apparently high variety of different palladium species. Existing methods are not only very time-consuming (due to necessary pre-separation procedures), there are also too few independent methods for validation of the results – even for the elevated palladium levels used in uptake studies. Up to now, speciation of palladium under non-exposed (‘natural’) conditions is hardly possible.

On the other hand, separation methods for Pd-species work quite well. Especially the combination of chromatographic and electrophoretic separations (GPC + ITP) is very promising, because these methods are complementary to each other, and make possible Pd speciation down to the ng- and even pg-range. Both methods can be used in preparative scale, and the risk of changing metal species is minimal.

The identification of separated species, which is always a key problem in speciation of trace and ultra-trace metals, has not been done yet for palladium species. Even with the most sophisticated mass spectrometric instruments there is at present no real chance to identify palladium species in separated fractions, which are in the pg-range for Pd. Maybe the investigation of metabolic profiles, e.g. by electrochemical monitoring of species patterns in relation to biological and environmental stress, could open an alternative way to answer biological questions, without the need to identify single species.

The few results, which have been obtained so far on palladium species in plants, do well correlate with the overall biological and toxicological effects, that have been reported in environmental monitoring and uptake studies. In particular, the higher toxicity and bioavailability of palladium (as compared to platinum and rhodium) correlates with the higher variety of respective palladium species.

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2.12 Analytical Procedure for the Quantification of *in vitro* Induced Pt- and Pd-DNA Adducts in Human Lung Cells

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Abstract

A combined analytical procedure is presented for the quantification of experimentally induced Pt and Pd DNA adducts in living cells by combining a DNA extraction technique with double focusing magnet sector field ICP-MS instrumentation. The proposed method is discussed in terms of possible spectral interferences, instrumental repeatability and experimental reproducibility. The statistical evaluation of a large dataset indicates that the method can be successfully used in experimental studies for the quantification of Pt and Pd DNA adducts.

Key words: Pt, Pd, DNA isolation, DNA adducts, HR-ICP-MS

2.12.1 Introduction

Since the mid 1980´s the platinum group elements (PGE) Rh, Pd and Pt are used as catalysts in converters to reduce the emission of different toxic gaseous compounds into the atmosphere, entailing the accumulation of large amounts of PGE in cities and along roads and highways with intensive traffic (Alt et al. 1997, Schäfer et al. 1997, Zereini and Alt 1998, Alt and Zereini 1999). Consequently, several studies document the contamination of different environmental compartments by these metals (for a recent review see Ravindra et al. 2004), but comparatively little is known about their mobility and speciation in the environment (Wei and Morrison 1994, Lustig et al. 1998, Menzel et al. 2001, Fliegel et al. 2004). Though the allergenic and cytotoxic property of Pt complexes and its binding ability to DNA is well documented due to the application of Pt compounds such as cisplatinum in cancer therapy (e.g., Hambley 2001, Cox et al. 2001, Natalie and Coluccia 2001, Silverman et al. 2002, Davies et al. 2003, Wheate et al. 2003), studies on the bio-availability and toxicity of PGE particles as emitted from catalytic converters are only sporadic (Bünger et al. 1996, Artelt et al. 1999). This kind of research is certainly hampered by the inherent analytical difficulties encountered in the quantification of very low PGE contents in relevant biological matrices (e.g, Begerow et al. 1997a, Zimmermann et al. 2001, Benkhedda et al. 2003, Betinelli et al. 2004).

Aiming to investigate the genotoxic effects of Pt and Pd on mammalian cells, we were faced with the problem to elaborate an adequate analytical procedure which combines the experimental generation and subsequent isolation of PGE-DNA adducts with a sensitive analytical step capable to reliably measure the low amounts of Pt and Pd bound to the genetic material. In this study we present a technique which allows the quantification of Pt- and Pd-DNA adducts generated by incubation of human lung cells with metallic PGE particles similar in size and composition to those emitted by cars equipped with PGE based catalytic converters. Toxicologycally relevant results, concerning the formation of Pt and Pd-DNA adducts will be presented elsewhere.

2.12.2 Materials and methods

Chemicals

For the generation of the PGE-DNA adducts metallic Pd (99.95% purity) and Pt powder (99.9%) were used (Alfa Aesar, Johnson Matthey, Karlsruhe, Germany), with a grain size of 0.25 – 0.5 and 0.2 – 1.6 µm, respectively, roughly similar to that of particles emitted by converters. Additionally, in some of the experiments cells were incubated also with Pt coated Al_2O_3 grains (< 5 µm) provided by the Frauenhofer Institute for Toxicology and Experimental Medicine in Hannover, Germany. This material, containing about 27-30 mg/g Pt was used as a model substance also by Artelt et al. (1999) in their study on the bio-availability of traffic emitted Pt. All organic compounds used for the isolation of DNA were at least of analytical grade. For mineralization of the isolated DNA and for all following steps only sub-boiled p.a. or suprapur quality HNO_3 and H_2O_2 (both from Merck) were used. Calibration solutions for the ICP-MS measurements were prepared from a PGE multi-element standard stock solution with 10 mg/l PGE dissolved in a 10 % v/v HCl (P/N 4400-ICPMS3, from CPI International). For dilution and washing solutions double distilled or deionised Milli-Q water (> 18 Mωcm^{-1}) was used.

Sample preparation

Cell culture and generation of the Pt- and Pd-adducts: The human adenocarcinoma cell line A549 was cultured in DMEM-Medium (10% FKS, 100U penicillin/ml and 100 µg streptomycin/ml) and grown as monolayer at 37°C in an atmosphere containing 5% CO_2 and 100 % humidity. Platinum and Pd treatments were performed in separate experiments. Before use, the respective metal powder was sterilized by incubation at 110°C dry heat for 20 min. A suspension was prepared by ultrasonicating the metal powder in sterile bidistilled water for 10 min (about 2-3 mg metal per ml H_2O).

Isolation of DNA: Following incubation the cells were washed with PBS four times, trypsinized and DNA was isolated according to Sambrock et al. (1989) with modifications (Schwerdtle et al. 2002). About 3 - 6 x 10^6 trypsinized cells were washed twice with ice-cold Tris-buffered saline (0.0027 M KCl, 0.137 M NaCl, 0.025 M Tris-base, pH 7.4) and collected by centrifugation. After 1 h incubation with extraction buffer (10 mM Tris-HCl, 0.1 M EDTA, 0.5% SDS, 20 µg/ml DNase-free RNase A, pH 8.0) at 37°C, proteinase K was added to a final concentration of 100 µg/ml and the suspension of lyzed cells was incubated at 50°C for 3 h. After cooling down to room temperature, DNA was extracted at least twice with phenol/chloroform/isoamyl alcohol (25:24:1; v/v/v) and once with chloroform/isoamyl alcohol (24:1). DNA was precipitated with ethanol/ammonium acetate and washed at least 4 times with 70% ethanol. The DNA concentration was determined spectrophotometrically by UV absorbance at 260 nm.

In order to exclude analytical artefacts due to an incomplete separation of the DNA from proteins or RNA, several approaches were applied to check the efficiency of isolation and to determine the purity of the isolated DNA. Among the different methods tested the A_{260}/A_{230} ratios proved to be the most convenient and to give reliable results with respect to DNA separation from proteins. Neither protein nor high-molecular RNA impurities as determined by RT-PCR (Reverse Transcription Polymerase Chain Reaction) were detected.

Sample mineralization: For quantification of metal contents with ICP-MS the isolated DNA was precipitated again with ethanol, washed four times and the DNA pellet was dried at ambient temperature for 4 h. Subsequently, a freshly prepared mixture consisting of 100 µl of HNO_3 (65 vol.%) and 100 µl H_2O_2 (30 vol.%) was added, kept 1 h at room temperature and incubated in an open vessel over night at 85°C. The dry residue was dissolved in 2 ml of 1 vol.% of HNO_3 immediately before the ICP-MS analysis.

2.12.3 Results and discussion

Quantification of the Pt and Pd concentrations by means of HR-ICP-MS

Instrumentation: ICP-MS proved to be an efficient and accurate method to quantify low concentrations of different PGE in biological samples (e.g., Begerow and Dunemann 1996, Begerow et al. 1997a, Krachler et al. 1998, Zimmermann et al. 2001, Bettinelli et al. 2004). The Pt and Pd concentrations in the mineralized DNA pellet were measured with a double focusing single collector ICP-MS (Axiom, VG Elemental, UK), equipped with a concentric Meinhardt type nebulizer (Glass Expansion, Australia; flow rate ~ 1.0 ml/min), impact bead spray chamber, standard quartz torch and Ni-cones. Instrumental settings were as follows: forward power ~1300 W, cooling gas flow rate ~ 13-14 l min^{-1}; auxiliary gas: ~ 0.60-0.65 l min^{-1}; nebuliser gas: 0.90–1.00 l min^{-1}; temperature of the spray chamber stabilized at ~10±1°C. Sensitivity (at a resolution of 400) varied on a daily basis between 4.0 to $6.0x10^5$ counts/second for 1 µg/l In (^{115}In).

Measurement technique: Concentrations were evaluated by external calibration at the beginning of each analytical session. Calibration solutions with 12.5, 25, 62.5, 125, 250 and 500 ng/l PGE (if necessary up to 1000 ng/l) were prepared in a 1 v/v% HNO_3 matrix to cover the whole range of the expected concentrations. The linearity of the calibration function as expressed by the correlation coefficient between signal intensity and concentration was always higher than 0.999 for all of the isotopes. Palladium was measured on the isotopes ^{105}Pd, ^{106}Pd and ^{108}Pd, while Pt on ^{194}Pt, ^{195}Pt and ^{196}Pt, registering 20 points per peak with a dwell time of 30 ms on each. Resolution was set to R=400. To correct for instrumental drifts and non-spectral matrix effects ^{169}Tm was used as internal standard. Reported concentrations (if not specified otherwise) are the average of three individual runs. Instrumental detection limit calculated on basis of repeated measurements of blank solutions (1 v/v% HNO_3 in deionised Milli-Q water) was found to be 15 ng/l for both elements (3 σ definition).

Spectral interferences: Both Pt and Pd isotopes can be affected by a series of spectral interferences in biological matrices (Krachler et al. 1998, Jensen et al. 2002). The isotopes ^{106}Pd and ^{108}Pd have isobaric interferences with Cd and ^{196}Pt with Hg, but the presence of these elements could not be detected in any of the measured samples. Among the argide clusters those derived from Cu ($^{40}Ar^{65}Cu$ for ^{105}Pd) and from Zn ($^{66}Zn^{40}Ar$ + $^{68}Zn^{38}Ar$ for ^{106}Pd and $^{68}Zn^{40}Ar$ for ^{108}Pd) are potentially the most severe, though they can be easily resolved at moderate to high resolutions ($R<7000$). Because several tests run at high resolution did not indicate the presence of such clusters all measurements were carried out at low resolution ($R=400$) in order to keep sensitivity as high as possible. The same is true for the HfO^+ clusters overlapping Pt isotopes, but which, if present, could have been resolved at $R<8800$. Oxide clusters interfering with the Pd isotopes, notably those from Sr, Y and Zr practically can not be kept apart. However, the count rates for the isotopes of these elements (^{88}Sr, ^{89}Y, ^{90}Zr) were found to be too low to represent a source for serious oxide interferences.

All the same, though at concentrations >50 ng/l Pd contents evaluated on basis of the three Pd isotopes agree within ± 5%, appreciable differences are noticeable below this value (Fig. 2.12.1a, 2.12.1b). This indicates that at very low Pd concentrations the influence of spectral interferences may not be completely neglected. Additional to the oxides already mentioned, the formation of chloride clusters, as suggested also by other authors (Jensen et al. 2003, Begerow et al. 1997b) should be considered. Despite thorough cleaning, due to the different Cl containing chemicals used in the separation of the DNA the presence of Cl clusters can not be excluded. Our tests show a linear increase of the count rates on masses 105, 106 and 108 parallel to increasing concentration of HCl in a 1 v/v % HNO_3 matrix (Fig. 2.12.2), suggesting the presence of clusters such as $^{35}Cl^{35}Cl^{35}Cl^+$ for mass 105, $^{35}Cl^{35}Cl^{35}Cl^1H^+$ or $^{35}Cl^{35}Cl^{36}Ar^+$ for mass 106 and $^{35}Cl^{35}Cl^{37}Cl^1H^+$ or $^{35}Cl^{37}Cl^{36}Ar^+$ for mass 108. Taking into account the natural abundance of the Cl isotopes, the ratio between the probabilities for the occurrence of the $3Cl\text{-}H^+$ clusters (106/108) can be evaluated. This can be done in a similar way also for the Cl-argid clusters. The average of the measured ratio in the HCl matrix of 1.071 ± 0.03 (1s) agrees roughly well with the theoretical value for the ratio between the $3Cl\text{-}H^+$ clusters (1.044), but not with that for the $2Cl\text{-}Ar^+$ clusters (1.57). Moreover, the ratio for the $2Cl\text{-}Ar^+$ clusters is much less then the range in which the ratios between the Pd concentrations ($^{106}Pd/^{108}Pd$) evaluated on the basis of these two isotopes scatter. Oxides should play a more important role in the occurrence of the interferences on the considered Pd isotopes than chlorides do. Due to the multitude of possibilities it is difficult to figure out exactly and to correct for these interferences. The lowest concentrations are given by ^{108}Pd, the highest by ^{106}Pd. This suggests the presence of SrO^+ species because the abundance of the SrO^+ cluster with mass 106 ($^{88}Sr^{18}O$) is about 2.5 times higher than that with mass 105 ($^{87}Sr^{18}O+^{86}Sr^{17}O$) and it is absent for mass 108.

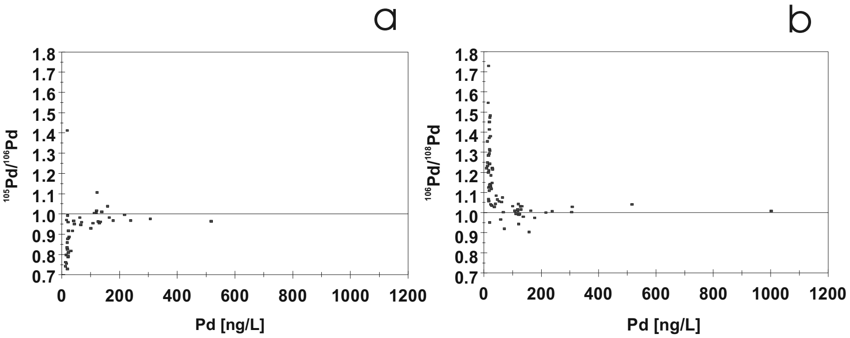

Fig. 2.12.1. Relative differences between Pd concentrations estimated on basis of different isotopes: (a) ^{105}Pd and ^{106}Pd and (b) ^{106}Pd and ^{108}Pd

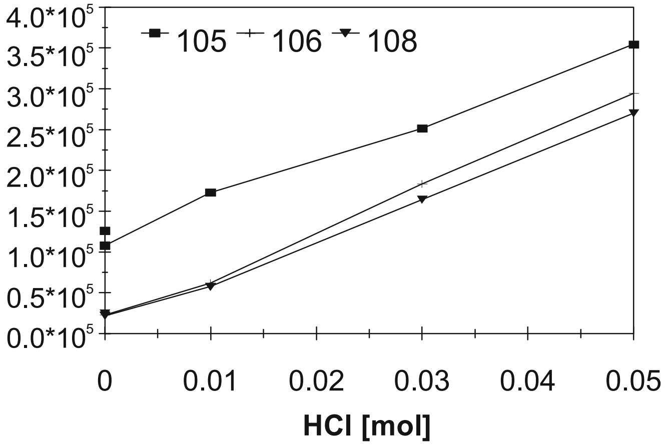

Fig. 2.12.2. Changes in signal intensity for mass/charge 105, 106 and 108 as a function of HCl concentration due to formation of clusters with Cl

The differences among the Pt contents evaluated separately on each of the monitored isotopes in 96% of the 238 measurements is less than ±5% and the concentrations do not correlate with the observed differences. Ratios between pairs of concentrations evaluated on basis of the three registered Pt isotopes are symmetrically distributed around a value of 1. These features indicate that there is no need to account for noteworthy isobaric interferences for Pt in the covered concentration range.

Instrumental analytical precision: Precision was estimated under repeatability conditions, i.e. the variance was assessed among independent results obtained under identical analytical conditions, within short intervals of time (Analytical Methods Committee, Royal Society of Chemistry 2003). Repeatability could be analysed in terms of two distinct sources of random errors: (i) variance due to short term changes in instrumental analytical conditions (as expressed by the variance of three consecutive runs) and (ii) variance mainly due to differences in the spectral interferences and in mass bias which affect each of the isotopes. Because at concentrations relevant for the experiments the ratio of the results based on the different isotopes of the element are distributed symmetrically around a value of 1 it can be assumed that this kind of error has for most of the measurements also a random character.

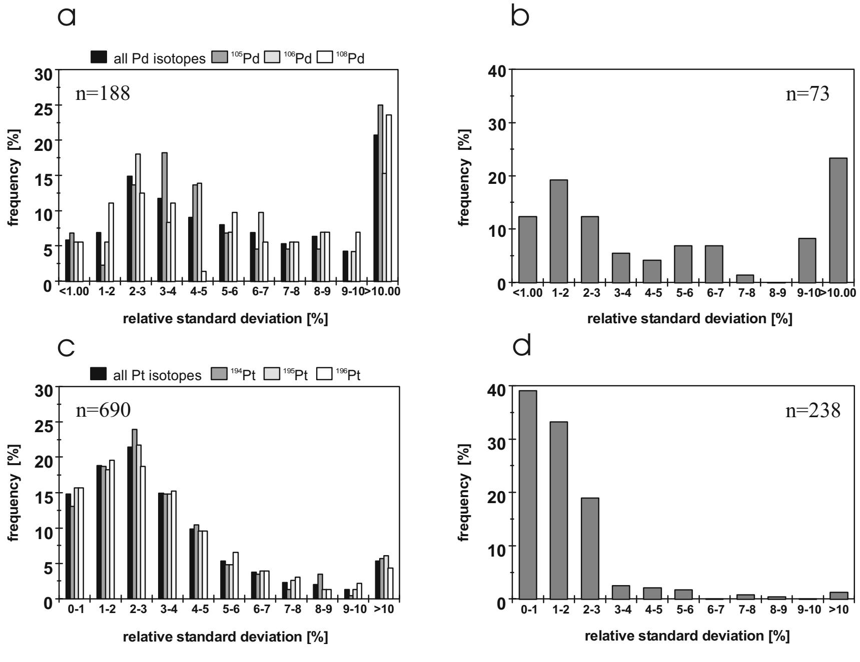

Fig. 2.12.3. **(a) and (c)**: Frequency distribution of relative standard deviations estimated from 3 individual runs for each of the isotopes and for all isotopes together. Frequency distribution of relative standard deviations estimated from three different isotopes of Pd **(b)** and of Pt **(d)**, respectively

The variance between the Pt concentrations estimated on basis of the three different isotopes (^{194}Pt, ^{195}Pt and ^{196}Pt) is very low (<3% for 91% and <5% for 96% of 238 individual measurements) (Fig 2.12.3d). Compared to this, the results for the different Pd isotopes scatter in a wider range, with only 44% of the data (from a total of 73 measurements) having a variance <3% (Fig. 2.12.3b). Additionally, for Pd there is a distinct subpopulation with high standard deviations which corresponds to the samples with Pd concentrations <50 ng/l. The heterogeneity of the Pd data is evidently due to the spectral interferences as discussed above.

The frequency distributions of the variances between individual runs for both elements are shown in Fig. 2.12.3a and 2.12.3c, separately for each of the isotopes and for all isotopes together. Compared to the inter-isotope variances the standard deviations are slightly higher in this case, for both of the elements. Only 55% of the Pt and 28% of the Pd data, respectively, have a relative standard deviation less than 3% (80 % of Pt and 48% of Pd have relative standard deviations < 5%). This suggests that the random error due to instrumental instability factors is higher for both elements than the error caused by randomly occurring spectral interferences. The difference between Pt and Pd in this respect is considerably less, except that again, the population with concentrations <50 ng/l on the Pd-histogram is clearly distinguished by high standard deviations.

Because final results are calculated as a combined average of both the mean of individual runs and mean of results on each isotope, the cumulated variance has to be considered to estimate the overall precision of the reported concentration values. The cumulated variance as a function of concentration is shown in fig. 2.12.4. If outliers are disregarded, precision apparently increases with increasing concentrations. Precision is better than 5% in 79% of the reported 230 Pt concentration values and in 94% of the cases the variance is less than 10%. Outliers are mainly due to unexpectedly high concentrations during the experiments which required extrapolation above the highest calibration point. For Pd, overall precisions are considerably worse, with only 1/3 of the values showing precisions better than 5%, while ¼ of the standard deviations are higher than 10%.

Quantification of the Pt and Pd adducts

Following the method of Reed et al. (1988) results are given as Pt and Pd adducts per 10^8 base-pairs. One femtomol of Pt or Pd per µg DNA corresponds to 66 Pt-adducts and 122.5 Pd-adducts per 10^8 base-pairs, respectively. The yield of the DNA extraction was determined by absorption photometry, using an Eppendorf „BioPhotometer“. The optical density was

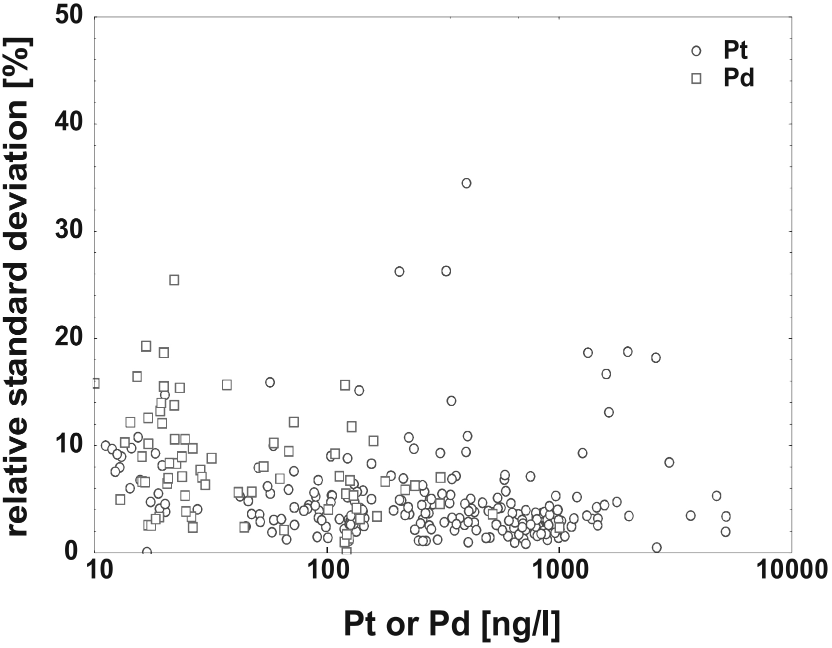

Fig. 2.12.4. Precision (expressed as relative standard deviation) of the ICP-MS measurements as a function of the Pt and Pd concentrations in the digested DNA pellets

measured at 260 nm in standard cuvettes (minimum volume 50 µl and optical path of 10 mm), at which an optical density of 1 corresponds to 50 µg DNA. Despite of some analytical drawbacks (Wilfinger et al. 1997) this technique was used because it is the only sufficiently sensitive and exact procedure for low sample volumes.

Procedural blanks (expressed as adducts per 10^8 base-pairs) were below 28 for Pt and below 63 for Pd. Despite exhaustive cleaning between individual measurements memory effects could not be completely eliminated. This makes a control of the blank values at regular intervals necessary.

Experimental reproducibility

In lack of appropriate certified standard materials a rigorous check of the accuracy could not be carried out. Spike recovery experiments could have been done only from the dissolution step of the DNA pellet which however are not of particular value because it does not cover the most critical step of DNA isolation. Nevertheless, testing the external reproducibility of the experimental results offers a reasonable mean to assess the reliability of the experimental data.

The arithmetic mean of three individual experiments after 24 h of incubation with 5 µg/cm² Al_2O_3-Pt particles is 3530±1520 (1σ) Pt-DNA adducts per 10^8 base pairs, while the incubation for 6 h with the same particle concentration yielded an average of 3180±1180 (1σ). Unfortunately, for Pd only two independent experiments could be carried out, so that the reproducibility turned out considerably worse: after 24 h and 6 h of incubation the number of Pd-DNA adducts per 10^8 base pairs was found to be 753± 659 and 752±691, respectively. In appraising these data on the reproducibility one should bear in mind that analyses on living biological systems are always more difficult to reproduce than such on non-living matter, especially in case of complex analytical procedures including several steps. The applicability of the procedure is strongly dependent on the total variance in the experimental data set.

2.12.4 Conclusions

The study demonstrates that Pt and Pd DNA adducts can be effectively quantified down to several tens of adducts per 10^8 base pairs by combining a standard DNA isolation technique (Schwerdtle et al. 2002) and open vessel acid digestion (HNO_3/H_2O_2) with ICP-MS as analytical instrument. Noteworthy spectral interferences were detected only for Pd at concentrations < 50 ng/L in the digested DNA pellet. These interferences are due to the formation of SrO^+ and possibly 3Cl-H^+ clusters. Overall analytical precision estimated from the combined variance between individual measurements on three different isotopes and between three individual runs is better than 5% for most of the Pt concentrations, but is considerably worse for Pd, with only 2/3 of the values showing precision better than 10%. Taking into consideration the difficulties in reproducing complex biological processes the achieved experimental reproducibility for Pt of ± 37 to 43% may be considered as satisfactory for many in vitro experimental studies.

Acknowledgements

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2.13 HPLC, Extraction and Solubilities of Pd (II) - und Rh (III)-Dialkyldithiocarbamates and Other Chelate Chemistry

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2.13.1 Introduction

Solubility is the deciding factor for any efficient extraction. Data of solubilities of chelates in $scCO_2$ are only available from very few authors. The vast majority of the solubility data for chelates in $scCO_2$ has been published by the working groups of Wai [2, 3], Erkey [4], as well as Taylor et al. [5].

The solubility can be increased considerably by the complete or partial substitution of the hydrogen by fluorine on the ligand [6]. The solubility of the Cu $(hfa)_2$ containing fluorine is for instance 211 times higher than the non fluorinated $Cu(acac)_2$ (at 200 bar and 40°C) [4]. The high price of the fluorinated ligands, due to their expensive production excludes the commercial use of this ligand group. Furthermore the fluorinated ligands are incompatible for the environment, thus causing additionally high expenses for their ecologically beneficial removal. Table 2.13.1 shows an overview of the solubilities in $scCO_2$ for some more common chelates. Non fluorinated β-diketones of 2,2,6,6-tetramethylheptandion (thd) show solubilities in the range of about $0.6 – 4.5 \cdot 10^{-3}$ mol kg^{-1} at 200 bar and 40°C. The solubility of the triple coordinated metal ions e.g. of the $Cr(thd)_3$ is about twice as high as that of similar doubly coordinated metal ions.

Most chelates of the acetylacetone have only small solubilties in the range of 10^{-8} - 10^{-6} mol kg^{-1}. The solubility of Palladium (II) -, Rhodium (III) - and Lead (II) – Diisopropyl-dithiocarbamate at different pressure and temperature-conditions and of some Palladium- and Rhodium-Chelates are reported by A. Wolf [7].

In general it is noticed that the influence of the central ion on the solubility is small, since the interaction solvent-solvens is primarily determined by the "ligand sphere" and the coordination number of the ion. The solubility of the chelates with the same ligand and the same coordination polyhedrons but with different central ions is therefore similar [8].

Table 2.13.1. Solubilities in $scCO_2$ of some selected chelates [1]

chelate	pressure in bar	temperature in °C	solubility in mol L^{-1}
Ni(Diethyldithiocarbamate)$_2$	100	50	$8{,}5 \cdot 10^{-7}$
Ni(Trifluorethyldithiocarbamate)$_2$	100	50	$7{,}2 \cdot 10^{-4}$
Zn(Dihexyldithiocarbamate)$_2$	100	60	$2{,}1 \cdot 10^{-4}$
Cu(acac)$_2$	103	40	$8{,}0 \cdot 10^{-6}$
Cu(hfa)$_2$	100	40	$2{,}2 \cdot 10^{-3}$
Cu(thd)$_2$	100	40	$6{,}2 \cdot 10^{-5}$
Cr(acac)$_3$	103	40	$1{,}7 \cdot 10^{-5}$
Cr(thd)$_3$	103	40	$4{,}0 \cdot 10^{-3}$
$UO_2(NO_3)_2 \cdot 2TBP$	101	40	$3{,}0 \cdot 10^{-3}$

Very high solubilities in $scCO_2$ are obtained by chelate formation with (sulphuric) organophosphorous ligands which dissolve almost unlimited in $scCO_2$ [9, 10]. The solubility of the copper with Cyanex-302 at 300 bar and 60 °C is 7.8 g L^{-1} [11]. The acid stability of these ligands allows to extract metal ions from very acidic solutions.

The best known extraction method with an organophosphorous compound is the extraction of Uranyl and Thorium ions with Tributylphosphate (TBP) from concentrated nitric acid which has been studied in detail by Wai et al. and which has been applied for US-Patent (as a replacement for the Purex method) [12, 13]. The extraction of Palladium, Platinum and Gold from concentrated hydrochloric acid, sulphuric acid and nitric acid with sulphuric organophosphorous compounds is possible. However it has only been described for the extraction of these metals in the µg-range [14, 15]. A further ligand group for the selective extraction of metal ions with $scCO_2$ are (fluorinated) crown-ethers and calixarenes [16]. It is possible to synthesize cavities of these macrocyclic multidental ligands for the chelate formation exactly to the radius of the metal ions [17]. Thus a high metal selectivity can be achieved with the extraction. It is for instance possible to extract selectively gold (III) ions from an aqueous solution with thiocarbamidecalix[4]arenes. However the difficult synthesis of the ligands is a severe handicap. Moreover the ligands can only be separated with great difficulties and not completely from the metal ions. This ligand group is therefore not appropriate for the extraction of chelates in the gram range.

It is also known that the solubility can be significantly increased by insertion of a neutral ligand into the coordination sphere of a chelate and by substitution of water molecules. Umland et al. [18] found out that minor additions of alcohols improve the solubility of magnesium oxinate, zinc oxinate or cadmium oxinate in chloroform. The tetrahedrally coordinated bivalent metal ions tend to change into octahedral complexes after the addition of water molecules. Thus the solubility in nonpolar solvents becomes very small. If the water molecules are now substituted by alcohols, a perceptible stabilization is found in nonpolar solvents.

2.13.2 Experimental

Problems of Chelate Analysis

The high stability of the chelates on the one hand and the tendency of the precious metal ions on the other hand to change to oxidation state (0) makes quantification of Rhodium and Palladium only possible after alkaline or acid oxidative digestion [19]. In order to determine Palladium or Rhodium chelates it is necessary to dry the chelate first, then digest the extracted chelates and then determine the metal. Each analytic step, shall introduce additional errors which shall reduce the precision of the analysis. Instead of elemental determination with the additional steps of digestion UV-VIS photometry offers a good alternative. It is non destructive and delivers results directly from the organic solvent at less analytic steps than element determination; however it is not element selective and not robust against influences of the matrix [20]. The quantification of the chelate extracts with UV-VIS spectroscopy can therefore only be employed with extracts of pure chelates.

The following methods for the quantification of chelate extracts have been applied:

- Direct gravimetric determination
  Pure chelates are extracted and collected in an extraction vial. The extracted chelate can be gravimetrically determined down to 1.0 ± 0.1 mg. Purity can be verified by the HPLC.
- Flame AAS determination of methanol dissolved chelate
  The absorbance of a methanolic solution of the chelate is measured after calibration of the flame AAS [21].

Table 2.13.2. Selected instrument setting for flame AAS of the Pd- and Rh-determination in methanol

element	wavelength (linear calibration 0...10 mg L^{-1})	wavelength (polyn. calibration function 10..100 mg L^{-1})	atmospheric pressure	acetylene pressure
Pd	247,6 nm	340,5 nm	1,6 bar	0,2 bar
Rh	343,5 nm	365,0 nm	1,6 bar	0,2 bar

Chelate Analysis with Flame-AAS in methanol solution

A Hitachi 180-70 flame AAS was available with combustion gas mixtures of acetylene (99.9996 %) and air. A strongly oxidizing flame was selected with an acetylene pressure of 0.2 bars and an air pressure of 1.6 bars. The intake rate of the vaporizer was then at about 4 mL min^{-1} for distilled water. Standard solutions were made from certified Rhodium- and Palladium-AAS standard solutions (Fluka) with a metal content of 1000 ppm in rectified methanol [22]. It became apparent that in particular the Palladium standard solutions in methanol were only stable in solutions for a period of 24 hours when a standard of Palladium(II)chloride in 10 % hydrochloric acid was used. Probably a reduction of Pd (II) to Pd (0) is prevented or slowed down within hydrochloric solution by the formation of palladium-chloro-complexes $[PdCl_4]^{2-}$. The element contents of the standard solutions depend on the content of the analysis and the selected measuring method.

A calibration range of 0.5 - 50 mg L^{-1} was accomplished after selection of appropriate instrument parameters. A linear calibration function was obtained up to 15 mg L^{-1}. Above 15 mg L^{-1} a second-degree polynomial calibration function had to be used. The appropriate Palladium-element line was selected according to the element content of the analysis.

For Palladium- and Rhodium-contents in the range of 10 - 100 mg L^{-1} the most intensive element line was not selected but one of smaller intensity line Table 2.13.2.

Halogenous solutions of the chelates could not be applied to flame AAS because the flame was extinguished.

HPLC

Freshly rectified, micro-filtrated (0.45 µm) methanol that had been degassed in an ultrasonico-bath (t >10 min) was used to study the retention reactions of the Dithiocarbamates. Acetonitrile (HPLC-grade, Promochem) was only degassed in the ultrasonic-bath and then used without microfiltration. A Lichrosphere RP 18 column (250 mm x 4.6 mm) from Merck with 7 µm particles and pre-column cartridge was used. At a flowrate of 1.0 mL min^{-1}, 20 µl of the samples were injected.

HPLC conditions are comparable to SFE conditions (high pressure, temperatures up to 80 °C; contact with metal surfaces). Thus important information can be attained concerning the stability of the chelates at high-pressure conditions. On the basis of the retention times also chelate polarities can be assessed [23, 24]. On a reversed-phase-HPLC column with relatively polar methanol as eluent is used, long retention time indicates, that the analyte is also relatively nonpolar and is thus probably soluble in $scCO_2$ [25].

Extraction studies of metal chelates with n-hexane were made according to the following procedure

5 mL acetic acid-acetate buffer solution pH = 4.75 are filled into a 250 mL shaking funnel. To this are added exactly 1 mL of a Palladium(II)chloride-standard solution (= 1 mg Pd) respectively 1mL of a Rhodium(III)chloride-standard solution (= 1 mg Rh) in 10% HCl and corresponding amounts of butanol and then this is shaken. Now exactly 1 mL of an 8-hxdroxychinoline solution (c = 4 g L^{-1}) in n-hexane is added, filled with n-hexane up to a total volume of 15 mL of organic phase (according to the volume of the additive) and shaken for three minutes. The aqueous phase is rejected. The organic phase is directly filtered through a folded paper filter into a 25 mL volumetric flask. The volumetric flasks are then filled up and measured with the UV-VIS-spectrophotometer Cary 50 in 1 cm cuvettes at 430 nm versus hexane.

2.13.3 FIAAS

Flow Injection Analysis

The metal contents of chelates in diluted chelate solutions can be better determined by flow-injection AAS (FIAAS) (sample volumes about 10 to 100 µL). The calibration of the AAS is made by the injection of different volumes of standard solutions and recording the absorption as a function of time. Fig. 2.13.1a) and 1b) shows the absorption signals of standard solutions and a characteristic calibration line of the flow-injection method. Further studies of the metal analysis of chelates with the flow method and the optimization of the analytic method are given by M. Gomes [26, 27].

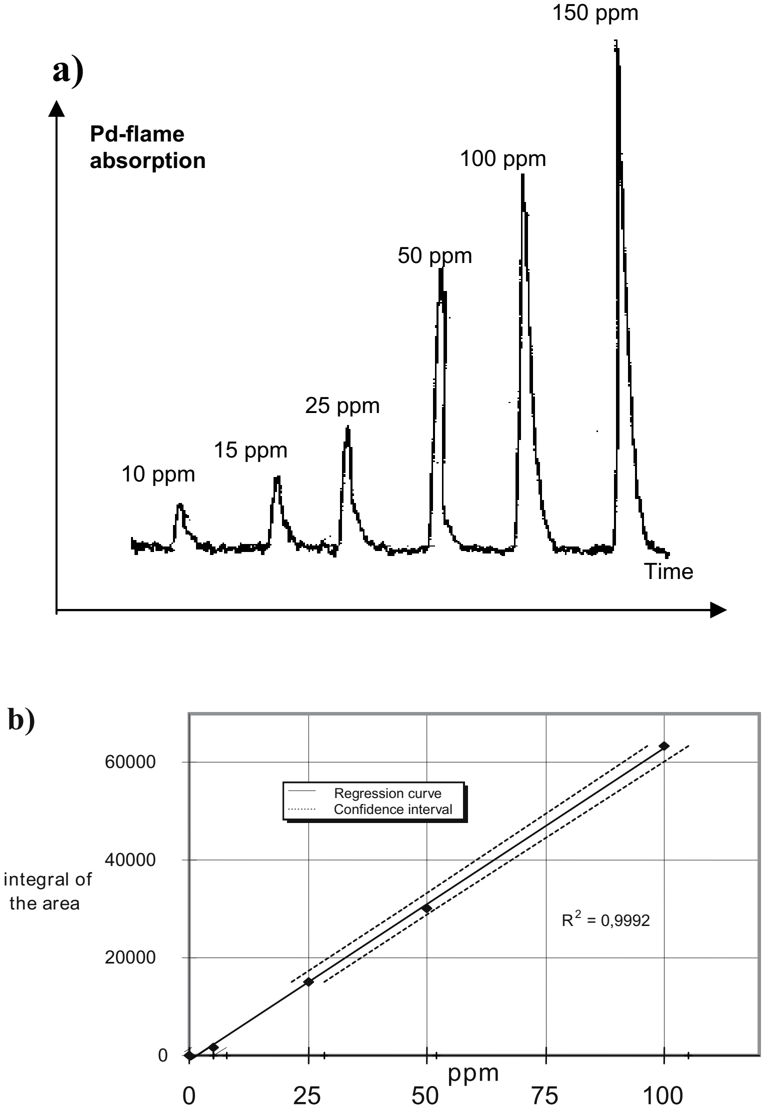


Fig. 2.13.1. a) FIAAS calibration of Pd-standard solution in diluted HNO_3 injection volume: 20 µL; Flow rate 2 mL min^{-1}
b) calibration curve with confidence interval (P = 99 %)

2.13.4 HPLC

Separation of homologous Pd(II)- and Rh(III)-Dialkyldithiocarbamates

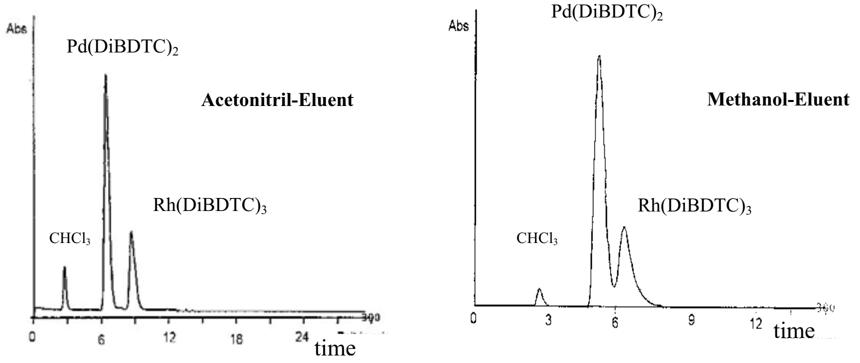


Fig. 2.13.2. HPLC of Pd- and Rh-Diisobutyldithiocarbamates dissolved in $CHCl_3^-$: Conditions: Flow rate 1,0 mL min^{-1}, Supersphere RP 18, UV detection 300 nm
a) Acetonitril, b) Methanol

HPLC columns with a packing material that had been modified on the surface with nonpolar C_{18}-(n- octadecyl-)-alkyl chains have proven to be suitable for the separation of most metal- Dithiocarbamates. Acetonitrile or methanol are appropriate eluents for the separation of homologous Palladium- and Rhodium- Dithiocarbamates on RPLC-columns. Acetonitrile causes a better resolution of the peaks (R = 2.6) at slightly longer retention times than methanol (R = 1.25) [28, 29] Fig. 2.13.2a) and 2.13.2b). The polarity of the eluent decreases by the addition of chloroform and thus reduces the retention time of the long-chain DTC-homologues.

The retention times of the long-chain DTC increase significantly by the addition of water (up to 5% by volume). However good chelate separations are obtained for chelates with an alkyl chain-length upto R = C_4.

Chelate Analysis with on line HPLC AAS

The hyphenation of flame AAS with RPLC allowed the element specific detection of different Palladium and Rhodium species within a chromatographically separated run or a metal analysis of the chelates dissolved in methanol by direct flow-injection.

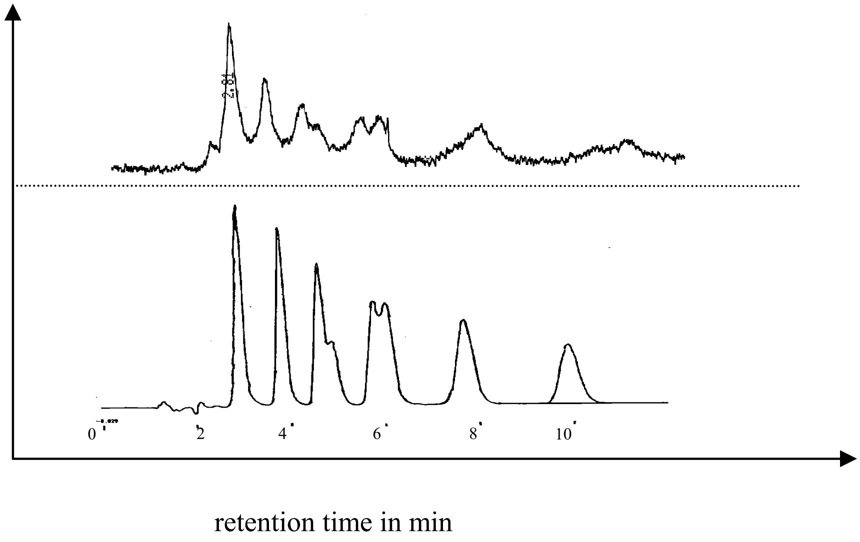


Fig. 2.13.3. HPLC separation of different Palladium chelate species on line AAS dtection, b) on line UV detection

For HPLC-AAS aliquots of the chelate solutions were injected into the column. The column outflow was directly connected to the nebulizer of the flame AAS. However due to the great dilution during HPLC, only concentrated chelate solutions can be detected on-line Fig. 2.13.3a) and 2.13.3b).

2.13.5 Influece of ligand side chains on retention times in HPLC

Retention times in HPLC

The retention times of the Dialkyldithiocarbamates also depend on the "history" of the column. After a regeneration of the column, the chelate sample had to be injected several times until the retention times remained constant. For an exact identification of any individual chelate in a mixture each chelate was also injected separately. Retention times of the Pd- Dithiocarbamates were always shorter than retention times of the corresponding Rh-Dithiocarbamates. Furthermore the Pd-DTC and the Rh-DTC with branched alkyl chains always elute earlier than the corresponding straight

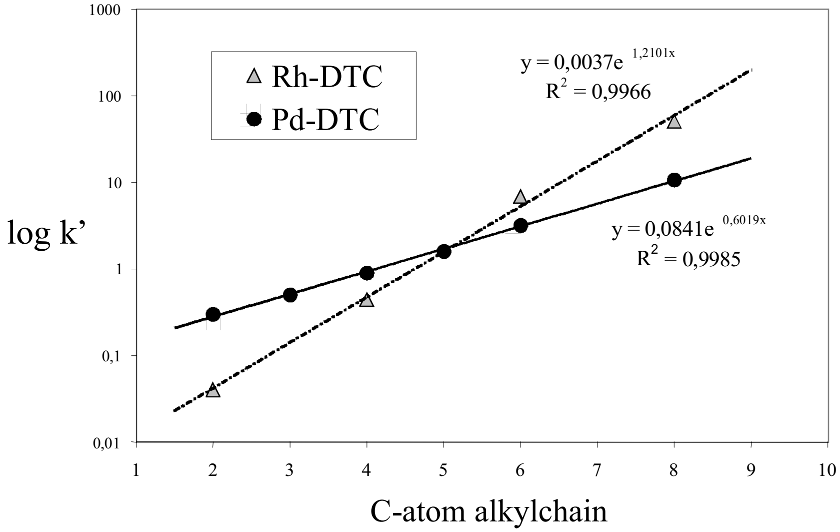


Fig. 2.13.4. Relationship log k\` versus carbon chain length for Pd and Rh DTC

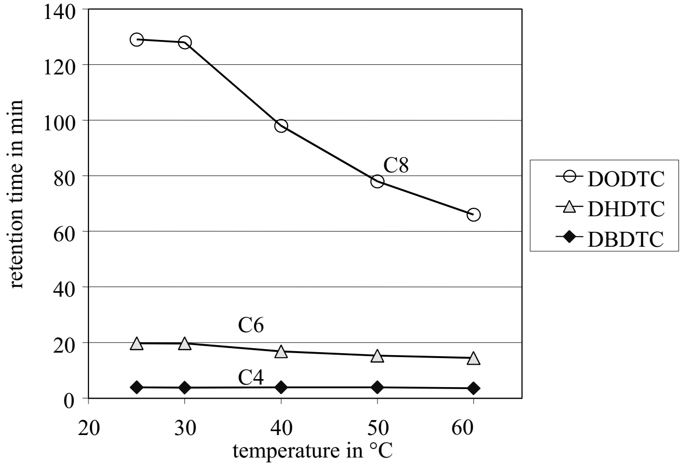
n-alkyl chelates. The retention times increase exponentially with increasing alkyl carbon chain. In Fig. 2.13.4 log k\` is plotted versus carbon chain-length and yields a straight line.

Influence of temperature on the retention time for chelates in HPLC

Before the solvent enters the column it was temperature equilibrated in a 1/6 capillary tube 2 feet long. The influence of the temperature on the retention of the Rh- and Pd- Dithiocarbamates is shown in Fig. 2.13.5a) and 2.13.5b).The retention time of the long-chain DTC is greatly reduced with increasing temperature of the eluent. An optimization of the separation of homologous metal-DTC by a temperature program as it is usual in gas-chromatography could also be applied here.

The pressure of about 200 bar and temperatures up to 70°C show no destructive influence on the Rh- and Pd-Dithiocarbamates. These conditions are well suited for SFE of the long-chain Rh- and Pd-Dithiocarbamates.

a) Rh



b) Pd

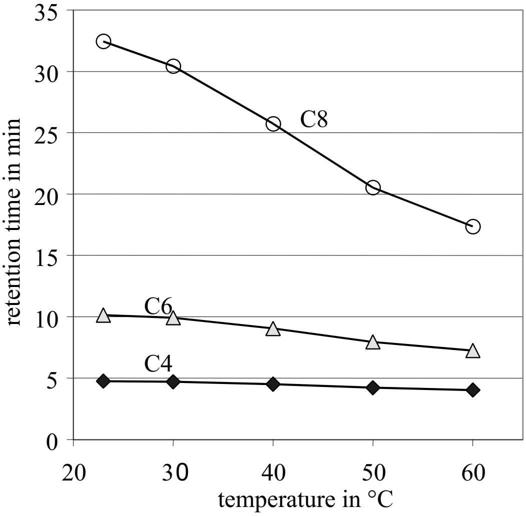


Fig. 2.13.5. Temperature dependence of the retetion time for homologous Dithiocarbamates
Conditions: mobile phase 100 % MeOH, Lichrosphere RP18, flow-rate 1,0 mL min^{-1}
a) Rhodium chelates b) Palladium chelates

2.13.6 Hexane Extraction

Hexane extraction of pure chelates

In order to assess the solubility of the chelates in $scCO_2$ first of all their extractability with n-hexane was studied. For this an excess (about 0.5 g) of the pure chelates was mixed in test tubes with exactly 5.0 mL of distilled n-hexane and the mixture was shaken and sonicated for 5.0 min each. Then it was left to rest for 48 hours at room temperature.

Table 2.13.3. ICP-AES metal content of the chelate extracts after aqua regia digestion and thereof calculated hexane solubilities

chelates	dissolved metal in mg L^{-1}	hexane solubility of the chelates in mol L^{-1}
β-diketonate		
$Rh(acac)_3$	77	$7,5 \cdot 10^{-4}$
$Rh(hfa)_3$	163	$1,6 \cdot 10^{-3}$
$Pd(thd)_2$	2597	$2,4 \cdot 10^{-2}$
$Pd(hfa)_2$	> 451	$> 4,2 \cdot 10^{-4}$
$Pd(acac)_2$	35	$3,3\ 10^{-4}$
oxinate (Ox)		
$Rh(Ox)_3$	(5)	$4,8 \cdot 10^{-5}$
$Pd(Ox)_2$	(1)	$1,3 \cdot 10^{-5}$
dialkyldithiocarbamate (DTC)		
$Rh(DiBDTC)_3$	39	$3,8 \cdot 10^{-4}$
$Rh(DBDTC)_3$	29	$2,8 \cdot 10^{-4}$
$Rh(DHDTC)_3$	8	$7,3 \cdot 10^{-5}$
$Rh(DODTC)_3$	17	$1,6 \cdot 10^{-4}$
$Pd(DiPrDTC)_2$	6	$5,5 \cdot 10^{-5}$
$Pd(DPeDTC)_2$	55	$5,1 \cdot 10^{-4}$
$Pd(DiBDTC)_2$	212	$2,0 \cdot 10^{-3}$
$Pd(DHDTC)_2$	22	$2,0 \cdot 10^{-4}$

2.0 (± 0.015) mL of this saturated hexane phase (with visible precipitate) were pipetted with an Eppendorf-pipette into a glas beaker. The hexane was vaporized in a nitrogen flow and the chelate residue was digested with 10.0 mL of hot aqua regia. ICP-AES was used for metal determination after dilution of the solutions with water to 100.0 mL. The metal content determined from the ICP-AES analysis and the calculated hexane solubilities of the chelates are compiled in Table 2.13.3.

$Pd(thd)_2$ and $Pd(hfa)_2$ show the highest solubilities in hexane. In order to assess the solubilty of $Pd(hfa)_2$ there was not enough substance to prepare a saturated solution, therefore only a minimum value for the solubility can be given. The 8-hydroxyquinolates are only weakly soluble in hexane. Dichlormethane or chloroform are much better solvents for the 8-hydroxyquinolates than hexane. Diisobutyl-residues deliver the best solubility of the DTC series. With shorter or longer alkyl-chains than R = 4 C, the hexane solubilities are smaller. The Diisobutyldithiocarbamates (DiBDTC) of the Rhodium are slightly better soluble than the Dibutyldithiocarbamates (DBDTC) of Palladium.

Hexane extraction of Rh 8-hydroxyquinolates with addition of n-butanol

An increase of the solubility of the Rhodiumoxinate was found after the addition of different amounts of n-butanol to hexane compared to of solubility in pure hexane Fig. 2.13.6.

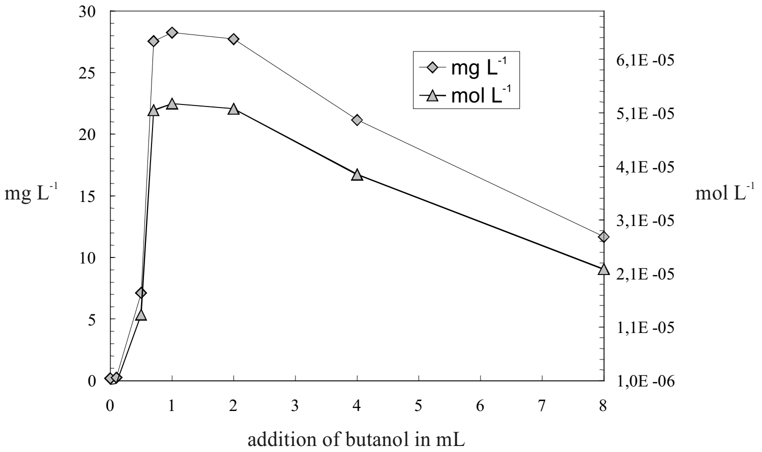


Fig. 2.13.6. Increase of the solubility of $Rh(Ox)_2$ in hexane after liquid-liquid extraction from an aqueous solution of n-butanol

2.13.7 Conclusion

A HPLC method for the separation of different Pd/Rh chelate species had been developed. Acetonitrile yields better resolution than methanol. As expected a linear correlation between log k` and carbon number were observed. Chelates with branched alkyl chains elute before the corresponding linear DTC.

All chelates were identified and characterized with optimized HPLC, UV-VIS spectroscopy, and elemental analysis.

A new flow-injection-AAS method for the direct metal analysis in methanol solution has been studied.

RPLC can be coupled on-line with AAS. The metal contents of the chelates was quantified with flame atom-absorption (FAAS) and with atomic-emission with inductively coupled plasma (ICP-AES).

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2.14 Analytical Methods to Determine Palladium in Environmental Matrices: A Review

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2.14.1 Introduction

Palladium is one of the platinum group elements (PGE_S) and it is present on the earth crust at very low concentration levels.

The members of PGE_S occur in nature as various mineral species, chiefly as antimonides, arsenides, bismuthides, sulfides, tellurides and in the native state (Reddi and Rao, 1999). The precious metals have some unique geochemical characteristics: they are very refractory, having high boiling points and a strong affinity for iron (siderophile) and for sulfur (chalcophile) (Goldschmidt 1954, Rösler and Lange 1972). They are normally present in silicate rocks at very low levels, often forming discrete phases, such as alloys and therefore, unlike the rare-earth elements, they do not appear to partition themselves extensively between silicate phases. It is therefore a critical task to select a representative natural sample mass for analysis, since the presence or absence of one precious metal grain in the analyzed aliquot could have a significant effect on the analysis, particularly if small sample masses (<5 g) are chosen. This inhomogeneity that is overall typical for the rock samples, might be taken into consideration by the analyst that generally are use to operate with samples of small size. In fact the homogeneity and the representativeness of the sample is the dominant factor to validate the analytical data on the real Pd distribution in environmental matrices (Hall *et al.* 1990; Reddi and Rao, 1999).

These considerations, together with the difficulties that arise applying analytical procedure owing to the very low Pd concentration in the environmental matrices, contrast with the large body of information concerning other metals of environmental significance such as Cd, Cr, Hg, Ni, Pb etc.

A significant collection of data on the environmental distribution of Pd and the consequent evaluation of the risks for human health and the environment from exposure to palladium are the results of the great effort of the Task Group on Environmental Health Criteria for Palladium (WHO, 2002).

Pd concentration in surface fresh water is generally detectable in the range from 0.4 to 22 ng L^{-1} in fresh water and from 19 to 70 pg L^{-1} in salty water. Drinking-water samples usually contain extremely low levels of palladium (few data always at a concentration level 24 ng L^{-1} are available in literature). A limited number of data are also available for Pd in tissues of small aquatic invertebrates, different types of meat, fish, bread and plants. Pd in soil range from < 0.7 to 47 μg kg^{-1} (WHO, 2002).

Soil samples were mainly collected from areas near major roads resulting enriched in this element.

Pd concentration in sewage sludge ranges from 18 to 260 μg kg^{-1}, while a very high concentration (4700 μg kg^{-1}) has been found in sludge samples contaminated by wastes discharged from the local jewellery industry (WHO, 2002).

Population is primarily exposed to palladium through different pathways that have different relevance: dental alloys, jewellery and metal refineries, food and emission from automobile catalytic converters (this one especially in the last decade). It is noteworthy to stress that at this time, at the relatively low concentration levels, metallic form of Pd and PGE$_S$ are considered to be inert respect to biological reactions (Ravindra *et al.* 2004).

The human average dietary intake of palladium has been calculated to be up to 2 μg/day. Ambient air levels of palladium below 100 pg m^{-3} can be expected in urban areas where palladium catalysts are used. Therefore, the inhalative palladium uptake rate is very low. In roadside dust, soil and grass samples a slight accumulation of palladium has been detected, correlating with traffic density and distance from the road (Zereini and Alt, 2000; Barefoot, 1999; WHO, 2002; Ravindra *et al.* 2004).

Worldwide demand for palladium in automobile catalysts rose from 23.5 tonnes in 1993 to 76.4 tonnes in 1996 (Cowley, 1997) up to 167 tonnes in 1999 (Ravindra *et al.* 2004). About 60% of the European gasoline cars present on the market in 1997 were equipped with palladium-based catalysts while in 2002 about 84% of the total Pd demand by application in Europe was employed for autocatalyst. The introduction of palladium in automotive catalytic converters in Europe during the early 1990s and the new catalyst introduced to satisfy the request of European legislation (Euro III and IV) have caused a growing demand for Pd. The consequence will be an increasing release and accumulation of this metal in the environment, paralleled by a reduction of Pt and Rh (Helmers *et al.* 1998; Hees, *et al.*1998; Schafer *et al.* 1999; Ravindra *et al.* 2004).

The production and recycling of Pd-containing materials, as well as the use of Pd as a constituent of dental restorative alloys, may be a source for toxic and allergic reactions for the organisms (Begerow *et al.* 1999; Begerow and Dunemann, 2000). A critical evaluation of possible risks for human health can only be given if reliable analytical data are available

(Messerschmidt *et al.* 2000). In fact, according to Boch *et al.* (2002), studies over the past 10 years have shown that the allergenic potential of palladium has been probably underestimated.

For this reasons it is important to develop analytical methods suitable for relatively easy determination of traces and ultra traces levels of Pd in the environment, as well as in body fluids of living species (Messerschmidt *et al.* 2000). Until now Pd has been preferentially determined in solid matrices as soils, sludge and dust, where is present at relatively higher concentration, while the paucity of data relatively for water system is related to the low levels and at the presence of salt that cause not easily resolved interferences. (Hall *et al.* 1990; Hall and Pelchat, 1993).

Terada *et al.* (1983) suggest that owing to these low concentrations in water, a preconcentration step is necessary. As an example, water insoluble chelating material (p-dimethylaminobenzylidenerhodanine on silica gel, or Thionalide) has been used for preconcentration of trace of palladium with a slow flow rate (2.5 mL/min).This have permitted the complete retention of palladium on the column. (Terada *et al.* 1980; Terada *et al.* 1983).

2.14.2 Analytical Procedures (solid matrices)

The analytical procedures for the determination of palladium (and other trace elements) can generally be divided into two main steps. The first is the sample decomposition (followed, if necessary, by a preconcentration step) in which these elements are separated from the host matrix and solubilised. In this step we can mention lead fire assay (Pb-FA), nickel sulphide fire assay (NiS-FA) and several wet chemical acid attacks (see Table 2.14.1). An other common dissolution method is fusion with lithium borates, sodium hydroxide and sodium peroxide, etc., again, if necessary, followed by a preconcentration step. Besides, the wet chlorination is another decomposition procedure, but generally limited to the analysis of precious metals.

The second step is the final instrumental determination. Several instrumental techniques are suitable for the measurement, such as flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS), neutron activation analysis (NAA), laser atomic fluorescence spectrometry with electrothermal vaporization (ETV-LAFS) and total reflection X-ray fluorescence (TXRF), adsorptive stripping voltammetry (ASV). A complete review of the analytical techniques for the determination of PGEs in geological and related materials was proposed by Reddi and Rao (1999).

2.14.3 Sample decomposition

Sample decomposition may involve three stages:

- reducing the solid sample to a homogeneous fraction;
- sample dissolution (followed, if necessary, by preconcentration step and elimination of interferences, according to the subsequent step);
- instrumental determination.

The development of a suitable method for digestion of a sample depends on:

i. the type of the sample material;
ii. the concentration of the analyte;
iii. potential contamination;
iv. availability of apparatus and reagents.

Table 2.14.1. Methods and analytical techniques for Pd determination in environmental matrices

Matrix	Extraction Method	Instrumental analytical method	Reference Material	L.O.D.	References
Airborne Particulate Matter	MW acid digestion	GFAAS		IDL: 0.06 μg/l (preconcentr. 3 ml of sample); IDL: 1.5 μg/l (for direct sampling)	Komarek et al. (1999)
	MW acid digestion (HNO_3/H_2O_2) and preconcentration on silica-gel (C18)	ICP-AES ICP-MS	NIES 8	IDL: ICP-MS: 0.09 ng/ml; ICP-AES: 5 ng/ml	Vlasankova et al. (1999)
	AR	GFAAS or LAFS			Tilch et al. (2000)
	MW acid digestion	Q-ICP-MS	NIST 2557; IMEP-11	IDL: 3.3 ng/l	Gomez et al. (2000)
	MW acid digestion (AR); residue: HCl treat.	ICP-MS LA-ICP-MS	NIST 2557		Rauch et al. (2001)
	acid digestion (HNO_3/HCl); concentration on C18 column; N,N-diethyl-N'-benzoylthiourea	GFAAS	BCR-723	MDL: 1.8 pg/m^3	Limbeck et al. (2004)

(Part 1 of 13)

Table 2.14.1. (cont.) Methods and analytical techniques for Pd determination in environmental matrices

Matrix	Extraction Method	Instrumental analytical method	Reference Material	L.O.D.	References
Airborne particles and road dust	MW acid digestion ($HCl/HNO_3/HF$)	HR-ICP-MS (UN)		MDL: 1pg/m3 (airborne); 2.5 ng/g (road dust)	Petrucci et al. (2000)
Airborne particles and road dust	MW acid digestion (AR/HF and AR/$HClO_4$)	ICP-MS; HR-ICP-MS; DP-CSV	CW7, CW8; NIST 2557; IMEP-11		Gomez et al. (2002)
	MW acid digestion (AR/HF) and Te coprecipitation	ICP-MS	CW7, CW8	MDL: 0.6 pg/m^3 (airborne); 1 ng/g (road dust)	Gomez et al. (2003)
Urban aerosol	MW acid digestion	ETAAS (online preconcentr.)	BCR-723	IDL: 23 ng/l; MLD: 4 ng/g	Limbeck et al. (2003)
	MW acid digestion followed by anion exchange	ICP-SFMS	BCR-723		Kanitsar et al. (2003)
Road dust	MW acid digestion (AR/HF/HCl)	ICP-SFMS	WPR-1	MDL: 0.54 ng/g	Koellensperger et al. (2000)
	MW acid digestion (AR/HF); followed by ion exchange	ID-ICP-QMS	WGB-1	MDL: 0.075 ng/g	Muller and Heumann (2000)
	MW acid digestion (HF)	ICP-MS; HR-ICP-MS; ID-ICP-MS; ETAAS			Schramel et al. (2000)
	MW acid digestion	GFAAS	NIES 8	IDL: 18 ng/l	Boch et al. (2002)
	MW acid digestion ($HNO_3/HCl/HF$); separation and concentration with polyacrolein-isonicotinic acid hydrazone resin	Q-ICP-MS	CW8		Ge et al. (2004)

(Part 2 of 13)

Table 2.14.1. (cont.) Methods and analytical techniques for Pd determination in environmental matrices

Matrix	Extraction Method	Instrumental analytical method	Reference Material	L.O.D.	References
Road dust	Hot digestion (AR) and Ion exchange with DOWEX-1-X10	ICP-AES		IDL: at λ 340.458: 0,019 µg/ml; at λ 363.47: 0.086 µg/ml	Kovacheva and Djingova (2002)
Road dust and road soil	MW digestion with AR; concentration and separation with exchange ionic column	ICP-MS	BCR-723	IDL 0,72 ng/l; MDL 12,93 ng/L	Whiteley and Murray (2003)
Road dust; atmosph. part.	MW acid digestion (AR)	Coupling IC and ICP-MS		IDL: 229.8 ng/l	Bruzzoniti et al. (2003)
Dust from leaves	Wet ashing; ionic exchange column	GFAAS			Hodge and Stallard (1986)
Street dust; plants:	Acid digestion, separation and concentration with solvent (ICP-MS); Dowex column 1X10-anion exchange (ICP-AES)	ICP-MS; ICP-AES	SARM-7; JSd-2	MDL: ICP-MS 0.01 ng/g; ICP-AES: 0.2 ng/g	Djingova et al. (2003a)
Urban road soil	NiS-FA	ICP-MS	SARM-7; WPR-1	MDL: 0.4 µg/Kg	Schafer and Puchelt (1998)
Urban road soil	MW Acid digestion HF/HNO3 and AR; Conc. cationic exchange resin	ICP-MS	UMT-1		Ely et al. (2001)
	Ashing at 450 °C; HCl/HF/HNO3 digestion and Te coprecipitation	ICP-MS	WPR-1	MDL: 0:088 ppb	Morton et al. (2001)
Urban road sediment	MW acid digestion (AR)	Q-ICP-MS LA-ICP-MS HR-ICP-MS	NIST 2557; IMEP-11		Rauch et al. (2000)

(Part 3 of 13)

Table 2.14.1. (cont.) Methods and analytical techniques for Pd determination in environmental matrices

Matrix	Extraction Method	Instrumental analytical method	Reference Material	L.O.D.	References
Urban road sediment	MW acid digestion (AR) for HR-ICP-MS	LA-ICP-MS; HR-ICP-MS	NIST 2557	MDL: 0.1-1 ng/g (HR-ICP-MS); 3-6 ng/g (UV-LA-ICP-MS); 3-14 ng/g (IR-LA-ICP-MS)	Motelica-Heino et al. (2001)
Soil, Road/ tunnel dust air partic. matter ash, mud	NiS-FA followed by wet chemical attack. For air partic. matter NiS-FA and Te coprecipitation.	Q-ICP-MS	SARM-7; WPR-1	MDL: 0.4 μg/kg	Schafer et al. (1999)
Urban lake sediment	NiS-FA	ICP-MS (SF-MCN)	BCR-723		Rauch et al. (2004a)
Car exhaust fumes	MW acid digestion; two steps procedures with AR/ HF and HNO_3/ HCl/ HF	ICP-MS	NIST 2557		Moldovan et al. (1999)
Car exhaust fumes; road dust	MW acid digestion (AR/ HF)	ICP-MS (MCN/DIN)		IDL (MCN): 8.8 ng/L; IDL (DIN): 5.8 ng/L	Garcia et al. (2001)
Automobile catalysts		GDMS	NIST 2556; 2557	Depends on the slit type and isotope: 0.064 - 23.3 μg/g	Wayne (1997)
	MW acid digestion	MC-ICP-MS	NIST 2556		Simpson et al. (2004)
Catalytic converters	Three differents procedures for acid digestion	ICP-MS	NIST 2557	IDL: 0.26 μg/l; MDL: 2 μg/g	Borisov et al. (1997)
	Alkaline fusion with Na_2O_2 at 750°C	ICP-MS			Amossé and Delbos (2002)
Deoxo catalyst	Hot digestion with HCl	DPV			Aher et al. (1999)
Automotive catalytic converter	Leaching and ion-exchange	ICP-AES			Gaita and Al-Bazi (1995)

(Part 4 of 13)

Table 2.14.1. (cont.) Methods and analytical techniques for Pd determination in environmental matrices

Matrix	Extraction Method	Instrumental analytical method	Reference Material	L.O.D.	References
Catalyst surface exhaust fumes	MW acid digestion (AR/ HF AR/$HClO_4$) with or without UV oxidation	Q-ICP-MS; HR-ICP-MS; CSV; Catal. surface: SEM/EDX, LIBS	NIST 2557 IMEP-11		Palacios et al. (2000)
Exhaust fumes, particulate and soluble fraction	Soluble sample: HCl (2%); particulate: AR/HF or AR/$HClO_4$ with or without UV oxidation	ICP-MS; HR-ICP-MS	NIST 2557; IMEP-11		Moldovan et al. (2002)
Catalytic converter and soil	NiS-FA	GFAAS	TDB-1; UMT-1; SARM-7		Zereini et al. (1997)
Automobile exhaust particles; road dust; river sediments	MW acid digestion (AR)	ICP-MS LA-ICP-MS			Rauch et al. (2002)
Road dust; urban river sediments	MW acid digestion (AR)	ICP-MS (UN)		MDL: 0.20 ng/g ^{105}Pd(LR); 0.30 ng/g ^{106}Pd(LR); 0.30 ng/g ^{105}Pd(HR); 0.25 ng/g ^{106}Pd(HR).	Rauch et al. (2000)
Spiked tap water and road dust	MW acid digestion, electrochemical preconcentration on a glassy carbon electrode	GFAAS		IDL: 0.05 ng/ml (1pg)	Godlewska-Zylkiewicz and Zaleska (2002)
Geological material	Hot AR digestion and alkaline fusion of residue	ICP- AES	PTA-1; PTC-1; PTM-1	IDL: 0.040 mg/L	Brown and Biggs (1984)

(Part 5 of 13)

Table 2.14.1. (cont.) Methods and analytical techniques for Pd determination in environmental matrices

Matrix	Extraction Method	Instrumental analytical method	Reference Material	L.O.D.	References
	NiS-FA	ICP-MS	SARM-7; PTC-1	IDL: 0.7ng/ml	Date et al. (1987)
	Acid dissolution and MIBK extraction	GFAAS	PTC-1	MDL: 3 ng/g	Brooks and Lee (1988)
	NiS-FA	NAA	SARM-7		Asif and Parry (1989)
	MW acid digestion (HNO_3/HCl/$HClO_4$) APDC complexation and MIBK extraction	GFAAS	GXR-1; PTC-1	MDL: 1 ng/g	Wilson et al. (1989)
	NiS-FA	AAS			Taufen et al. (1989)
	Acid dissolution and ion exchange or Te coprecipitation	GFAAS	SU-1a; PTC-1; PTM-1; PTA-1; SARM-7; DZE-1; DZE-2; W-1; DTS-1; PCC-1; AGV-1;		Sen Gupta (1989)
	NiS-FA	ICP-MS	SARM-7; PTC-1; SU-1a		Jackson et al. (1990)
	Hot partial digestion by HCl, HNO_3 and reductive coprecipitation (Hg)	GFAAS	SARM-7	MDL: 0.5 µg/kg	Niskavaara and Kontas (1990)

(Part 6 of 13)

Table 2.14.1. (cont.) Methods and analytical techniques for Pd determination in environmental matrices

Matrix	Extraction Method	Instrumental analytical method	Reference Material	L.O.D.	References
Geological material	Acid digestion (AR)	ICP-MS	SARM-7; PTA-1; PTC-1; PTM-1; SU-1a; GXR-1; GXR-4		Gowing and Potts (1991)
	FA	NAA	SARM-7; MA1b	MDL: 0.025 mg/kg	Asif et al (1992)
	NiS-FA	ICP-MS	SARM-7; CHR-Pt+; CHR-Bkg	IDL: 0.015 ng/g; MDL: 1.11 ng/g	Juvonen et al. (1994)
	NiS-FA	NAA	SARM-7		Schmidt and Pernicka (1994)
	NiS-FA and Te coprecipitation	ICP-MS	SARM-7 (MSPT-1 in-hause standard)	MDL: 0.5 ng/g	Reddi et al. (1994)
	MW acid digestion and alcaline fusion of the residue	ICP-MS	MA-2a; PTM-1; SARM-7; SU-1a; 2/77		Totland et al. (1995)
	MW digestion, alkali fusion and cation exchange chromatography	ICP-MS	MA-2a; PTA-1; PTC-1; PTM-1; SARM-7; SU-1a;	MDL: 11 ng/g	Jarvis et al. (1997)
	Alkaline fusion	NAA	W-1; PCC-1; DTS-1		Ahmad et al . (1977)
	8 steps preliminar separation for speciation study. NiS-FA preconcentration	ICP-MS	GPT-2, GPT-4		Li et al. (1998)

(Part 7 of 13)

Table 2.14.1. (cont.) Methods and analytical techniques for Pd determination in environmental matrices

Matrix	Extraction Method	Instrumental analytical method	Reference Material	L.O.D.	References
Geological material	Alkaline fusion	LA-HR-ICP-MS	UMT-1; WPR-1	MDL: 7 ng/g	Shibuya et al. (1998)
	MW acid digestion (HF/ HNO_3) and concentration with cationic exchange resin	UN-ICP-MS	UMT-1	MDL: fg/g 594 (external calibration) and 2188 fg/g (with standard addition)	Ely et al. (1999)
	NiS-FA and Te-coprecipitation	ICP-MS	SARM-7; 2/77; WPR-1; UMT-1; WMG-1	IDL : 0.11 ppt; MDL : 9 pg/g	Oguri et al. (1999)
	Carius tube digestion, solvent extraction and anion-exchange chromatog.	ID-ICP-MS	WITS-1	MDL: 5 pg/g	Pearson and Woodland (2000)
	HPA-S digestion (HNO_3/HCl)	ICP-MS	UB-N; KAL-1; WGB-1; TDB-1; UMT-1		Meisel and Moser (2004)
	NiS-FA	ICP-MS	TDB-1; WPR-1; WMG-1		Zhou et al. (2001)
	NiS-FA	NAA and UV-LA-ICP-MS	UMT-1; WMG-1; GPt-4; GPt-6	MDL: 1.4 ng/g (LA-ICP-MS); MDL: 6 ng/g (INAA)	Figueiredo et al. (2000)
	MW Acid digestion	ICP-MS (ID)	CHR-BKg; TDB-1; WGB-1	IDL: 0.18 ng	Meisel et al. (2001)
Sulfur-poor rocks	Alkaline fusion and Te-coprecipitation	RNAA	W-1; MKV; PCC-1; SCo-1	MDL: 0.3 ppb	Stone and Crocket (1993)
Minerals (diabase)	Pb-FA	GFAAS			Gottfried et al. (1990)

(Part 8 of 13)

Table 2.14.1. (cont.) Methods and analytical techniques for Pd determination in environmental matrices

Matrix	Extraction Method	Instrumental analytical method	Reference Material	L.O.D.	References
Basalt (oceanic)	MW acid digestion (HF/ HNO_3);concentration cationic exchange. resin	ICP-MS	UMT-1		Ely and Neal (2003)
Geolog. samples CRM; Road dust; Plant leaves	MW acid digestion	ICP-MS	SARM-7; JSd-2	MDL: 0.015 ng/g	Djingova et al. (2003b)
Rock, soil, sediment	Pb-FA	NEB-ICP-MS	TDB-1; WGB-1; WPR-1; WMG-1; WMS-1; UTM-1	IDL: 0.02 μg/l; MDL: 0.5 ppb	Hall and Pelchat (1994)
Marine sediments	Acid dissolution (HNO_3/ HF) and MIBK extraction	GFAAS		MDL: 0.2 ppb	Terashima et al. (1993)
Ores and rock	NiS-FA	LA-ICP-MS	SARM-7, 2/77, CHR Pt+	MDL: 10-90 ng/g	Jarvis et al. (1995)
Rock and ores	NiS-FA and Te-coprecipitation	NAA	SARM-7	MDL: 7μg/kg	Shazali et al. (1987)
	MW acid digestion ($HNO_{3/}$HCl and addit. step with HF). Dissolution Residue Na_2O_2 and dynamic sorption, with EDTA.	ETAAS	SARM-7	MDL: 5×10^{-7}%	Kubrakova et al. (1996)
Silicate rocks	Hot acid dissolution with HF and AR followed by preconcentration on ionic exchange column	GFAAS with Zeeman background correctiom	SU-1a; PTM-1; UMT-1		Sen Gupta (1993)
	Alkaline fusion anionic resin exchange (in batch)	GFAAS	SARM-7		Enzweiler and Potts (1995)

(Part 9 of 13)

Table 2.14.1. (cont.) Methods and analytical techniques for Pd determination in environmental matrices

Matrix	Extraction Method	Instrumental analytical method	Reference Material	L.O.D.	References
Soil	Acid digestion (AR)	ICP-MS		MDL: 10 µg/g	Cicchella et al. (2003)
	NiS-FA	INAA		MDL: 0.3 ng/g	Heinrich et al. (1996)
	Hot acid digestion (AR/HF/HCl). Metal complexation and organic extraction	GFAAS			Patel et al. (2000)
Volcanic Fluids		ICP-MS (SF)		IDL: 4.440 ng/l ; MDL 1.110 µg/l	Fischer et al. (1998)
Geol. and biol. materials; dust plants; water;	Alkaline fusion, clhorination, acid digestion, fusion, slurries	LA-ICP-MS, GFAAS, INAA	SARM-7; PTC-1; SU-1a; NMB 6a; CHR-Pt+; CHR-Bkg	MDL: 0.1 ng/g (geological material with Pb-FA)	Perry et al. (1995 a)
Rock samples; GSO-Au-2; Yangxin copper ore (spiked Pd)	Hot acid digestion	AAS on-line column with the FI		IDL: 0.3 ng/ml	Lin et al. (1995)
Water solution	AR digestion; complexes (DEDTC) Solvent extraction	HPLC (UV detection)		IDL: 0.5 ng/ml	Mueller and Lovett (1985)
Synthetic samples and alloy	Acid digestion and hot complexation with Salicylaldehyde tris(hydroxymethyl)methylamine	Polarography			Sreenivasulu et al. (1985)
Sinthetic solution	MW acid digestion (HF/AR)	IDMS offline anion echange	WPR-1; CW-8	MDL: 25 ng/g (procedure 1) MDL: 2.8 ng/g (procedure 2)	Hann et al. (2001)

(Part 10 of 13)

Table 2.14.1. (cont.) Methods and analytical techniques for Pd determination in environmental matrices

Matrix	Extraction Method	Instrumental analytical method	Reference Material	L.O.D.	References
Idrogenation catalyst; Biolog. sample	On-line column preconcentration and separation system	GFAAS		IDL: 13-51 ng/l	Schuster and Schwarzer (1996)
	Hot AR	UV-Vis Spectrofotometry	NIES 8 (Vehicle exhaust particulates), NIES 7 (Tea leaves), NIES 2 (Pond sediment)	IDL: 17 ng	Pancras and Puri (1999)
Sea water; Biol. and Geol. samples	Acid digestion and preconcentration with a-benzildioxime	NAA	SARM-7; PCC-1; SU-1a; SRM 1566; SRM 1573; SRM 1575	IDL: 10 ng	Bem and Ryan (1985)
Sea water	Preconcentration DMABR on silica gel	AAS			Terada et al. (1980)
	Preconcentration Thionalide on silica gel	AAS			Terada et al. (1983)
	Preconcentration complex Pd-DMG	ASV			Wang and Varughese (1987)
Sea water; waste water; sediment; Pt & Ag metals; Biol. materials	Liquid samples: direct filtration, fotochemistry oxidation with HCl-H_2O_2. Solid sample: Hot HNO_3/H2SO_4/H_2O_2.	ASV	NIST 1567; NIST 1568; NIST 1577A; NIST 1572; NIST1633	MDL: Liquid samples 0.05 µg/l; Solid samples 50 ng/g	Georgieva and Pihlar (1997)

(Part 11 of 13)

Table 2.14.1. (cont.) Methods and analytical techniques for Pd determination in environmental matrices

Matrix	Extraction Method	Instrumental analytical method	Reference Material	L.O.D.	References
Urban waters	On-line preconcentrated on alumina microcolumns	ICP-MS		IDL: 1 ng/l	Moldovan et al. (2003)
Polar and alpine snow and ice	HNO_3 acidification	DF-ICP-MS-MN*		MDL: 0.08 pg/g	Barbante et al. (1999)
Ice and snow	HNO_3 acidification	DF-ICP-MS		MDL: 0.09 pg/g	Van de Velde et al. (2000)
Fresh snow	HNO_3 acidification	DF-ICP-MS-MCN	SLRS3		Veysseyre et al. (2001)
Fresh water	absorption onto activated charcoal	NEB-ICP-MS ETV-ICP-MS		MDL (NEB): 0.8 ng/l; MDL (ETV): 0.3 ng/l	Hall and Pelchat (1993)
Biological materials	Hot acid digestion (HNO_3/H_2O_2) and dilution with H_2O and tiourea	ETAAS		IDL: 15 pg/ml	Ohta et al. (1996)
Asellus aq. (urban river)	MW acid digestion	ICP-MS	NIST SRM-2557; IMEP-11		Moldovan et al. (2001)
Plant tissues	NiS-FA	NAA			Dunn et al. (1989)
Vegetation ash	Hot HF/AR digestion and Te coprecipitation	GFAAS; ICP-MS		IDL: 2ppb (Neb-ICP-MS); 1 ppb (GFAAS); 0.3 ppb (ETV-ICP-MS)	Hall et al. (1990)
Arctic vegetation	Hot HF/AR digestion and Te coprecipitation	ICP-MS		MDL: 0.5 ppb	Rencz and Hall (1992)

(Part 12 of 13)

Table 2.14.1. (cont.) Methods and analytical techniques for Pd determination in environmental matrices

Matrix	Extraction Method	Instrumental analytical method	Reference Material	L.O.D.	References
Plants	MW digestion HCl/ HNO_3/ HF and Te coprecipitation	ICP-MS		MDL: 2.50 µg/g (for 2g ashed plant material); 0.72 µg/ g (for 7g plants)	Schafer et al. (1998)
Pine needles	Alkaline fusione and acid digestion at 95° (HNO_3+HCl)	ICP-MS		MDL: 3ng/g	Dongarrà et al. (2003)
Ombrotropic peat bog	NiS-FA	XRF and ICP-MS	BCR-723		Rauch et al. (2004b)
Urine; air; road dust	Acid digestion with reductive coprecipitation with mercury	TXRF		IDL: 2.5 ng/l (20 ml urine); 50 pg (absolut amount)	Messerschmidt et al. (2000)
Urine	UV irradiation or acid digestion	Q-ICP-MS; HR-ICP-MS with UN	NIST 2670	IDL: 0.25 ng/l	Krachler et al (1998)
Sinthetic solutions	Digestion with AR	IC		MDL: 1ppb	Rocklin (1984)
Human blood	HNO_3 at 50°C for 30'	ICP-MS			Begerow et al. (1997)

(Part 13 of 13)

MDL: method detection limit; IDL: instrumental detection limit; MW: microwave oven; AR: aqua regia; FAAS: flame atomic absorption; GFAAS: graphite furnace atomic absorption spectrometry; ICP-MS: inductively coupled plasma mass spectrometry; ICP-AES: inductively coupled plasma atomic emission spectrometry; IDMS: isotope dilution mass spectrometry; GDMS: glow discharge mass spectrometry; ASV: adsorptive stripping voltammetry; NAA: neutron activation analysis; TXRF: total reflection X-ray fluorescence; DPT: differential pulse voltammetry; LIBS: laser induced breakdown spectrometry; DF: double focusing; NEB: nebulization; ETV: electrothermal vaporization; MN: microconcentring nebulization; UN: ultrasonic nebulization; MC: multi-collector; HPA-S: High pressure asher.

NIST 1567 (Wheat flour); NIST 1568 (Rice flour); NIST 1577A (Bovine liver); NIST 1572 (Citrus leaves); NIST1633 (Bowen's Kale; Coal fly ash). SLRS3 (riverine reference material for trace metal) UB-N (peridotide); KAL-1 (Komatiite);
NIES 8 (Vehicle exhaust particulates), NIES 7 (Tea leaves), NIES 2 (Pond sediment)

A wide range of digestion methods have been developed for the analysis of geological and related materials, with dissolution routinely accomplished by acid attack at atmospheric or elevated pressures (Totland *et al.* 1995). Extensive reviews of digestion procedures are given by Bock (1979) and Sulcek and Povondra (1989), while general overviews are provided by Potts (1987) and Jarvis (1991), the last two pertaining specifically to ICP techniques. A clear distinction should be made between methods in which the entire sample is dissolved and methods in which the elements of interest are extracted from bulk sample by acid leach, leaving the majority of the sample undigested.

Brown and Biggs (1984); Hodge *et al.* (1986); Sen Gupta (1989); Sen Gupta and Gregoire (1989) investigated acid attack to digest a range of materials prior to PGE determination, and observed that generally the dissolution was incomplete, so they used an alkali fusion to digest the refractory phases of samples

2.14.4 Acid Dissolution

Wet chemical attack forms an important and widely followed method for precious metal determinations. The efficiency of different acid leaching mixtures has been studied extensively as a dissolution step prior to the determination of the PGE's. Various acids have been used, including ratios of HCl and HNO_3 (Parker and Murray Smith, 1979; Niskavaara and Kontas, 1990) HCl and H_2O_2.

Perry *at al.* (1992, 1995 b) have investigated dry-chlorination as a means of converting the PGE present in geological samples (native metals, natural alloys and PGE-bearing sulphide group minerals) into sodium salts then dissolved in weak HCl. But by far the most popular reagent for leaching the PGEs is aqua regia (Palmer *et al.* 1971; Bowditch, 1973; Branch and Hutchinson, 1986; Grote and Kettrup, 1987; Gowing and Potts, 1991; Nowinski and Hodge, 1994; Cinti *et al.* 2002).

Sometimes aqua regia could be an ineffective leaching mixture: in particular when a significant fraction of these elements may occur as solid particulate, within refractory silicate minerals, after the dissolution and when PGEs are present in discrete, potentially soluble mineral grains, but these are in resistant matrix phases such as chromite (Totland *et al.* 1995). The same author reported an interesting application of mixed acid digestion procedure, followed if necessary by the alkali fusion of insoluble residues.

Palladium, in contrast to other platinum group elements, binds strongly to silicate residues even in acid solutions (Boch *et al.* 2002). As several investigations have experimentally evidenced (Totland *et al.* 1995; Borisov *et al.* 1997) the analysis of palladium in solutions containing silicate residues always produces inconsistent results. Therefore the silicate containing samples must be digested completely: this requires the application of oxidizing acids as well as hydrofluoric acid (Boch *et al.* 2002).

Serious problems, however, arise also employing multi-acid digestion procedures. This problems are related to variation and heterogeneity in particle size (Potts, 1987), difference in sample matrix composition and incomplete wetting as well as the different used experimental conditions. An important prerequisite to obtain reproducible data employing wet chemical attack is to obtain uniformity in sample mesh size e.g. 200-250 (but it is highly advisable to lower as much as possible the particle size); otherwise, within the grains of the host matrix, discrete noble metal minerals may be completely occluded and not be fully dissolved by acids (Reddi and Rao, 1999). Nevertheless acid extraction of palladium results to be a more rapid and economically alternative to fire assay. Usually, additional preconcentration steps are needed prior to the determination of the analytes after acid treatment. The results for a variety of samples have not always been quantitative and depend upon the type of samples as well as the experimental conditions. Other significant factor that influence the effectiveness of acid dissolution techniques is the ratio between sample weight and the volume of acid.

As final consideration, wet chemical attack has the following advantages: a) low cost, b) low blanks, c) amenability for batch analysis and d) it is ideal for semiquantitative data generation for exploratory work (Reddi and Rao, 1999).

For organic matrices as blood UV photolysis has been found to be advantageous over conventional mineral acid digestion techniques. The use of minimal reagent addition permits to obtain extremely low blank values. Besides, in contrast to acid dissolution, any large dilution of the sample solution is necessary (Begerow *et al.* 1997).

2.14.5 Fire Assay

Among the analytical procedures developed to determine the PGEs in geological samples, fire assay with nickel sulphide followed by an analytical detection technique with high sensitivity is one of the most accepted (Asif and Parry, 1989; Shibuya *et al.* 1998).

The precious metals are often present in rocks and ores at very low levels and their distribution can be very inhomogeneous. These two factors favour the fire-assay approach where a large sample can be used and where the precious metals are concentrated into small buttons or beads.

The two dry assay procedures, Pb-FA and NiS-FA, after separation from the slag, result in buttons of manageable proportions amenable for easy manipulation. The other decomposition methods, multi acid decomposition, fusion, etc., quite often necessitate of separation and preconcentration steps.

The technique of fire assay involves fusing together a sample and a flux at a temperature of about 1000°C. The resultant melt separates into two immiscible phases. Aluminosilicates and base metals are contained in the lighter glassy slag that will be discarded, whereas nickel sulphide button that represents the more dense collector phase, mainly composed by molten lead , is collected at the bottom. So the noble metals and, among these Pd, result strongly partitioned into this collector phase from which they may be subsequently separated for analysis (Reddi and Rao, 1999). NiS-FA presents some advantages respect to Pb-FA. These can be summarized as follow:

a) reduced modifications in the flux compositions are required even if there are differences in sample types; b) any preliminary removing of nickel and sulphur is required; c) large sample sizes can be used because higher fluxes are employed; d) the NiS button is suitable for laser ablation studies.

Instead the disadvantages of the NiS fire assay can be summarized as:

a) the relatively high cost; b) an efficient fume and gas extraction needs because large amount of hydrogen sulphide gas evolved during the treatment of the NiS button with hydrochloric acid; c) the large quantity of reagents used could add impurities and an overestimation of the PGEs if not fully considered (Reddi and Rao, 1999); d) the large amount required for the sample could be a restriction for some environmental matrices.

2.14.6 Analytical Techniques

Because the concentration of PGE_S is generally very low in environmental compartments, their quantification requires analytical techniques with a high sensitivity, selectivity and that permit the control of the possible interference effects. To overcome this analytical challenge few analytical techniques are directly applicable. In many case preconcentration and/or separation of the analyte from the matrix are required.

The most useful analytical detection techniques for the determination of these elements after solubilization and, if necessary, pre-concentration are atomic absorption spectrometry (AAS), neutron activation analysis (NAA), inductively coupled plasma spectrometry (ICP-MS) and, sometimes, inductively coupled plasma atomic emission spectrometry (ICP-AES) (Shibuya *et al.* 1998).

2.14.7 Atomic Absorption Spectrometry (AAS-GFAAS)

For many years, both FAAS and GFAAS have been popular instrumental methods for determinations of many elements. Graphite furnace AAS, offers the unique advantage of enhanced sensitivity over the flame version. The detection limits are thus lowered by at least one to two orders of magnitude depending on the element and sample volume. Thus GFAAS competes favourably in terms of detection limits with other sensitive techniques such as NAA and ICP-MS in palladium determination (Komarek et al. 1999, Boch et al. 2002, Zereini et al. 1997, Patel et al. 2000)**.** The major disadvantages, however, are the inherently lower productivity and more severe interferences (Reddi and Rao, 1999).

2.14.8 Neutron Activation Analysis

NAA is a very sensitive and versatile multi-element technique, allowing analysis of solid (Asif and Parry, 1989) or liquid samples (Asif *et al.* 1992) samples. In the case of NiS buttons, the mass of the collector material must be lower than 0.5 g, since Ni provides high background activity on irradiation, causing problems related with the reproducibility (Asif and Parry 1989, Jackson *et al.* 1990). A limitation of this technique is the cost that it is a very expensive and time consuming one (Shibuya *et al.* 1998). This technique, based on the reaction with thermal neutrons ^{108}Pd(n,Y) ^{109}Pd, which produce ^{109}Pd ($t_{1/2}$=13.6 h), has been extensively used to quantify palladium. However, because of the low energy of emitted Y-rays (88 KeV) and high Compton background in that region, instrumental (non-destructive) N.A.A. can be applied only to samples which have a high concentration of palladium. Usually, a preconcentration step for removal of the main constituents of the matrix or separation of palladium after irradiation is necessary for samples which have a palladium content below 1 mg Kg^{-1} (Bem and Ryan, 1985). Many interesting study were exploited on palladium determination by NAA using different procedures for samples digestion. Good agreement were obtained using certified material. (Shazali et al. 1987, Asif and Parry 1989, Stone and Crocket 1993 and Figueiredo et al. 2000).

2.14.9 Inductively Coupled Plasma MS or AES

Plasma spectrometry has been widely employed for the major, minor and trace elements analysis of several types of geological materials. ICP-MS achieves lower detection limits than ICP-AES, being more suitable for trace analysis and is generally capable of determining Pd down to the pg range (Krachler *et al.* 1998; Rodushkin *et al.* 1999). However, this technique suffers from spectral interferences (Evans and Giglio 1993) adding to the general problem linked to the partial insolubility of most samples. Regarding not-interfered isotopes, sector field ICP-MS operating in the low resolution (LR) mode permits far better detection limits than with quadrupole instruments when using a comparable sample introduction system (Moens *et al.* 1995; Begerow, 1996).

As already discussed, PGEs do not always have a homogeneous distribution along the matrix (Chen *et al.* 1997): dissolution procedures are time consuming and, in addition, sample can be contaminated and composition changed by losses of some of the volatile elements. As a consequence, it could be desirable to avoid such procedures by using direct measurement techniques (Shibuya *et al.* 1998). In recent years, the laser ablation technique coupled with an inductively coupled plasma mass spectrometer (LA-ICP-MS) has been developed as a powerful tool for the direct analysis of solid samples (Gray 1985; Russo 1995; Longerich, *et al.* 1993). This technique offers the possibility for the direct analysis of trace elements in solid materials and provides for a rapid characterization of different types of environmental samples, eliminating complex separation procedures and drawbacks of solution analysis which include potential contamination by chemical reagents, loss of volatile elements and dilution of the analytes. A further advantage of LA-ICP-MS is the production of a dry plasma reducing the formation of interfering oxides and hydroxides which are undesirable, because the laser beam is focused on the surface of a solid sample producing a fine particles mixture and a vapour for analysis. This technique can be used as a rapid characterization technique for urban air particulates collected on filters and might be a suitable technique for the determination of trace elements in sediments (Shibuya *et al.* 1998; Motelica-Heino *et al.* 2001; Rauch *et al.* 2001).

Table 2.14.2. Isobaric interferences for Pd determined by ICP-MS. (Garcia *et al.* 2001; Bencs *et al.* 2003)

Analyte	Analyte abundance (%)	Interferent Ion species	Interferent abundance (%)	Required Resolution (Δm/m)
^{102}Pd	1.02	$^{86}Sr^{16}O^+$	9.84	71713
		$^{204}Hg^{++}$	6.85	1257
		^{204}Pb	1.37	1261
		^{102}Ru	31.60	80780
^{104}Pd	11.14	$^{40}Ar^{64}Zn^+$	48.41	8500
		$^{38}Ar^{66}Zn$	0.02	6200
		$^{36}Ar^{68}Zn$	0.06	9000
		$^{40}Ar^{64}Ni$	0.90	7900
		$^{88}Sr^{16}O$	82.36	33500
		$^{87}Sr^{17}O$	0.003	23600
		$^{86}Sr^{18}O$	0.02	21200
		$^{87}Rb^{17}O$	0.01	22100
		$^{208}Pb^{2*}$	52.38	1200
		$^{104}Ru^*$	18.7	54700
^{105}Pd	22.33	$^{40}Ar^{65}Cu^+$	0.003	7300
		$^{36}Ar^{69}Ga$	0.20	92000
		$^{89}Y^{16}O^+$	99.76	27600
		$^{88}Sr^{17}O$	0.03	1000000
		$^{87}Sr^{18}O$	0.014	30900
		$^{87}Rb^{18}O$	0.056	28400
^{106}Pd	27.33	$^{40}Ar^{66}Zn^+$	27.79	7200
		$^{38}Ar^{68}Zn$	0.013	6800

(Part 1 of 3)

Table 2.14.2. (cont.) Isobaric interferences for Pd determined by ICP-MS. (Garcia *et al.* 2001; Bencs *et al.* 2003)

Analyte	Analyte abundance (%)	Interferent Ion species	Interferent abundance (%)	Required Resolution ($\Delta m/m$)
		$^{36}Ar^{70}Ge$	0.02	9300
		$^{90}Zr^{16}O^+$	51.30	26500
		$^{106}Cd^+$	1.25	27900
		$^{89}Y^{17}O$	0.037	58800
		$^{88}Sr^{18}O$	0.16	70600
		$^{87}Rb^{18}O^1H$	-	-
		$^{40}Ar^{65}Cu^1H$	-	-
^{108}Pd	26.46	$^{40}Ar^{68}Zn^+$	18.72	6500
		$^{40}Ar^{72}Ge$	0.005	7300
		$^{40}Ar^{68}Zn$	18.7	6500
		$^{92}Zr^{16}O^+$	17.06	540000
		$^{92}Mo^{16}O^+$	15.00	40000
		$^{108}Cd^+$	0.89	1080000
		$^{38}Ar^{70}Ge$	0.014	8600
^{110}Pd	11.72	$^{36}Ar^{74}Ge$	0.12	7000
		$^{38}Ar^{72}Ge$	1.90	5300
		$^{36}Ar^{74}Se$	0.003	7300
		$^{40}Ar^{70}Ge^+$	21.44	6000
		$^{92}Zr^{18}O$	0.034	78500
		$^{94}Zr^{16}O^+$	17.30	26800
		$^{92}Mo^{18}O$	0.03	366000
		$^{94}Mo^{16}O^+$	9.33	20000

(Part 2 of 3)

Table 2.14.2. (cont.) Isobaric interferences for Pd determined by ICP-MS. (Garcia *et al.* 2001; Bencs *et al.* 2003)

Analyte	Analyte abundance (%)	Interferent Ion species	Interferent abundance (%)	Required Resolution (Δm/m)
		$^{93}Nd^{17}O$	0.037	323251
		$^{110}Cd^{+}$	12.49	52300
		$^{40}Ar^{70}Zn$	0.004	216000

(Part 3 of 3)

UV laser ablation HR-ICP-MS technique seem be a very promising analytical tool for determination of PGEs in geological materials and in comparison to IR laser ablation quadrupole permit to achieve higher sensitivity and better detection limits.

Regarding to the ultratrace determination of Pd by ICP-MS, spectral interferences are the principal limitation degrading the detection limits in real matrices. As it has already been evidenced in several literature papers, the determination of Pd in the lower ng L^{-1} range can be affected by several spectral interferences represented by the species Pb^{2+}, SrO^{+}, RbO^{+}, ZrO^{+}, $CuAr^{+}$, $ZnAr^{+}$ and Cd^{+} (Begerow and Dunemann 1996, Gray and Williams 1987). An exhaustive list of spectral interferences on Pd are reported in Table 2.14.2.

The formation of Cl_3^{+} is another potential polyatomic ion of relevance in chloride containing matrices, such as blood, interfering with the Pd determination at m/z 105 (Jarvis, 1991). Measurement of NaCl solutions evidence the formation of Cl_3^{+}: after subtraction of the blank of ultrapure water, 1 g L^{-1} of NaCl solution caused a signal at m/z 105 equivalent to 15 g L^{-1} of Pd, mainly consisting of the Pd blank of NaCl and the Cl_3^{+} interference. As a conclusions the chloride content of the sample solution has to be kept as low as possible (Begerow *et al.* 1997).

Unfortunately many of these interferences cannot be eliminated even by using a magnetic sector field ICP-MS instrument in the high resolution (HR) mode because the high resolution of the instrument (up to m/Δm ≈7500) is not sufficient to separate Pd isotopes from spectral interferences such as those of $^{104}Ru^{+}$, $^{88}Sr^{16}O^{+}$, $^{106}Cd^{+}$, $^{108}Cd^{+}$ and Cl_3^{+}. Moreover, the sensitivity at a resolution of m/Δm ≈7500 is about 1% of that obtained working a resolution of m/Δm ≈300 lowering, as a consequence, the detection limits. The removal of interfering elements by suitable sample preparation steps seems again to be preferable even working in the HR mode if close to the detection limits.

The spectral interferences could be eliminated in the high resolution mode by applying a mathematical correction (Krachler et al. 1998; Rodushkin et al. 1999). However, because interferences can affect rather all Pd isotopes, for each matrix it is needed to chose the most abundant and less interfered Pd isotope. So a preliminary study of the matrix occurs. As an example Krachler et al. (1998) have studied the concentration range of potential interfering elements on ^{106}Pd in urine.

An other relevant problem in PGEs determination with ICP-MS is the formation of double charges that reduce the detection limit and produces interferences. Because the formation of double charges depends by many parameters, they can be minimized but not fully avoided. An exhaustive discussion on this important problem can be found on the paper of Pupyshev and Semenova, (2001).

2.14.10 Total Reflection X-ray Fluorescence

Applying the previous discussed analytical techniques a direct determination of Pd is possible only in a limited number of cases because very often an additional separation or enrichment step is necessary. Mathematical correction method is suitable for the determination of Pd in body fluids (complex but compositionally constant matrices) but cannot be always easily applied for the environmental samples such, as an example, road dust owing to the complexity and variability of the matrix (Lustig et al. 2000).

To overcome interference troubles in Pd determination, Messerschmidt *et al.* (2000) have used the total reflection X-ray fluorescence technique (TXRF) with a procedure based on a reductive coprecipitation of Pd with mercury. According to the authors the main advantage is the almost complete separation of the analytes from the matrix and the high degree of enrichment, thus enabling a determination without interferences at highest sensitivity. The detection limit in about 2 ng L^{-1}. However this method is time consuming and it may serve mainly as an independent method in order to control other analytical techniques.

2.14.11 Voltammetry

Owing to the irreversibility of the electrode processes, measurement of Pd by electrochemical methods results rather difficult. Polarographic and related techniques have shown that the reduction of Pd becomes faster in complex forming media. Further increase of the sensitivity and selectivity of ASV (Anodic Stripping Voltammetry) and other advanced electroanalytical techniques can be achieved by the modification of the electrode and/or an enhanced adsorption of reactants. Ligands containing oxime groups, well known from their use in gravimetric analysis, are often used for the adsorptive accumulation of Pd on Hg electrodes. Wang and Varughese (1987) elaborated a very sensitive ASV method based on the pre-concentration of Pd-dimethylglyoxime complex on a hanging Hg electrode which is a promising approach for the determination of ultra-trace Pd levels, permitting a LOD of 20 ng L^{-1}.

2.14.12 Certified Reference Materials

Standard and certified reference materials (SRMs, CRMs) are very important because they provide a tool to check accuracies of new procedures. The recent demand by the exploration community for improved methods by which to determine Pd in variety of matrices has clearly demonstrated the inadequacy of the available reference material for this element (Hall and Bonham-Carter, 1988). So, at the present time, there is an evident need for environmental reference materials containing certified low levels of Pd (Perry et al. 1995a).

The majority of available reference materials refers different type of minerals, ore, etc. (such as SARM-7), recycled monolith autocatalyst (NIST- 2557) or car exhaust catalyst material (IMEP 11), where the concentration of PGE are considerably higher (in the higher mg Kg^{-1} range) than those typical of environmental materials (normally µg Kg^{-1} and lower), and the matrix composition and forms of PGE are very different. Thus, the methods validated against these CRMs may not necessarily provide reliable data in the case of road dust, soils, sediments and plants (Djingova et al. 2003b).

To fill this gap, there are several existing and well-established geological RMs. These have not been prepared specifically for use as PGE RMs or are prepared as in house PGE standards, which are now used for assessing repeatability within a laboratory.

Since these RMs are not certified for PGE, they are not useful for detecting bias. Therefore, small round robin tests have been launched to establish a means of detecting and understanding between laboratory differences (Meisel and Moser 2004).

Tables 2.14.3 and 2.14.4 shows a collection of commonly used certified reference materials, together with other reference samples which were not originally prepared for PGEs certification but have been also analysed for these elements.

Table 2.14.3. Reference Materials analysed for Pd. Certified, indicative and found value are expressed in $\mu g\ L^{-1}$

RM Certified or indicative value	Method	Instrumental technique	Found value	References
SARM-7 1530 ± 32	NiS-FA	ICP-MS	1320 ± 60 1353 ± 142 1507 ± 75 recovery 90-97% recovery 90-97%	Date et al. 1987; Jackson et al. 1990; Juvonen et al. 1994; Schafer and Puchelt, 1998 Schafer et al. 1999
		NAA	1497 ± 100 1537 1350 ± 270	Schmidt and Pernicka, 1994 Shazali et al. 1987 Asif and Parry., 1989
		LA-ICP-MS	1360-1410	Jarvis et al. 1995
		GFAAS	1460 ± 98 1200 (Te coprecipitation)	Zereini et al. 1997 Sen Gupta, 1989
	Aqua regia	ICP-MS	1180	Gowing and Potts, 1991
	Acid-dissolution	ICP-MS	1520 ± 25 1580 ± 110 (cation-exchange sep.) 1530 ± 32 (MW - AR/HF) 1230 ± 95 (residue fusion)	Djingova et al. 2003b Jarvis et al. 1997 Totland et al. 1995 Totland et al. 1995
		NAA	1590 ± 50	Bem and Ryan, 1985
		GFAAS	1490 ± 20	Niskavaara and Kontas, 1990
	Sodium peroxide fusion	GFAAS	~70-80% (several method)	Enzweiler and Potts, 1995

(Part 1 of 8)

Table 2.14.3. (cont.) Reference Materials analysed for Pd. Certified, indicative and found value are expressed in $\mu g\ L^{-1}$

RM Certified or indicative value	Method	Instrumental technique	Found value	References
PTC-1 12700 ± 700	NiS-FA	ICP-MS	6870 ± 180 11438 ± 412	Date et al. 1987; Jackson et al. 1990;
	Aqua regia	ICP-MS	6010	Gowing and Potts, 1991
PTC-1 12700 ± 700	Acid-dissolution	ICP-MS	12200 ± 1400 (cation-exchange sep.) 11100 ± 1200 (with fusion of residue)	Jarvis et al. 1997 Totland et al. 1995
		GFAAS	11000 (Te-coprecipitation) 11300 (ion-exchange) 12850 ± 560 (extraction with MIBK) 12440 ± 248	Sen Gupta , 1989 Sen Gupta , 1989 Brooks and Lee,1988 Wilson et al. 1989
PTM-1 8100 ± 700	Aqua regia	ICP-MS	5	Gowing and Potts, 1991
	Acid-dissolution		9300 ± 1300 (cation-exchange sep.) 9600 (MW with HNO_3/HCl/HF/$HClO_4$) 7600 ± 120 (residue fusion)	Jarvis et al. 1997 Totland et al. 1995 Totland et al. 1995
		GFAAS	7000 (Te-coprecipitation) 8000 (ion-exchange) 7800	Sen Gupta , 1989 Sen Gupta , 1989 Sen Gupta, 1993
SU-1a 370 ± 30	Aqua regia	ICP-MS	265	Gowing and Potts, 1991

(Part 2 of 8)

Table 2.14.3. (cont.) Reference Materials analysed for Pd. Certified, indicative and found value are expressed in $\mu g\ L^{-1}$

RM Certified or indicative value	Method	Instrumental technique	Found value	References
	Acid-dissolution	ICP-MS	300 ± 40 (cation-exch. sep.)	Jarvis et al. 1997
			610 (MW with $HNO_3/HCl/HF/HClO_4$)	Totland et al. 1995 Totland et al. 1995
			400 ± 50 (MW AR/HF)	Totland et al. 1995
			560 ± 110 (residue fusion)	
		GFAAS	340 (Te-coprecipitation)	Sen Gupta , 1989
			400 (ion-exchange)	Sen Gupta , 1989
			360	Sen Gupta, 1993
SU-1a 370 ± 30		NAA	310 ± 30	Bem and Ryan, 1985
	NiS-FA	ICP-MS	327 ± 27.47	Jackson et al. 1990
BCR-723 6.0 ± 1.8	Acid dissolution	ICP-MS	5.86 ± 0.33 (cation exchange)	Whiteley and Murray, 2003
		ICP-SFMS	4.9 ± 0.7	Kanitsar et al. 2003
		GFAAS	5.3 ± 2.0	Limbeck et al. 2003
	NiS-FA	ICP-MS (MCN)	6.6	Rauch et al. 2004a
		ICP-MS	within 20%	Rauch et al. 2004b
JSd-2 21.2	Acid dissolution	ICP-MS	21 ± 2 (DDTC complex, extraction with chloroform)	Djingova et al. 2003b
PTA-1	Acid dissolution	ICP-MS	470 ± 100 (cation-exchange sep.)	Jarvis et al. 1997
			450 ± 180 (residue fusion)	Totland et al. 1995
		GFAAS	20 (Te-coprecipitation)	Sen Gupta , 1989
			<100 (ion-exchange)	Sen Gupta , 1989
	Aqua regia	ICP-MS	16	Gowing and Potts, 1991

(Part 3 of 8)

Table 2.14.3. (cont.) Reference Materials analysed for Pd. Certified, indicative and found value are expressed in $\mu g\ L^{-1}$

RM Certified or indicative value	Method	Instrumental technique	Found value	References
MA-2A	Acid dissolution	ICP-MS	340 ± 70 (cation-exchange sep.) <1100 (MW with HNO_3/ HCl/HF/$HClO_4$) 860 (with fusion of residue)	Jarvis et al. 1997 Totland et al. 1995 Totland et al. 1995
UMT-1 106 ± 3	NiS-FA	LA-ICP-MS	108 ± 14 113 ± 6	Shibuya et al. 1998 Figueiredo et al. 2000
		GFAAS	130 ± 6	Zereini et al. 1997
UMT-1 106 ± 3		ICP-MS	95.6 ± 3.7 (Te-coprecipitation)	Oguri et al. 1999
		INAA	90 ± 18	Figueiredo et al. 2000
	Pb-FA	ICP-MS	104 ± 10	Hall and Pelchat, 1994
	Pb-FA	See Ely et al. 99 See Ely et al. 99	102.1 97.8 ± 10.7	Ely and Neal, 2003 Ely et al. 2001
	Acid solution	GFAAS	93	Sen Gupta, 1993
		ICP-MS (UN)	101.7 ± 23	Ely et al. 1999
WPR-1 235 ± 9	NiS-FA	LA-ICP-MS	249 ± 42 170 ± 30	Shibuya et al. 1998 Figueiredo et al. 2000
		ICP-MS	233 ± 17 (Te-coprec.) recovery 90-97% recovery 90-97% 208.7 ± 7.1 (Te-coprec.)	Zhou et al. 2001 Schafer and 7Puchelt, 1998 Schafer et al. 1999 Oguri et al. 1999
		INAA	235 ± 42	Figueiredo et al. 2000
	Pb-FA	ICP-MS	246 ± 15 Lab1; 247 ± 11 Lab2	Hall and Pelchat, 1994

(Part 4 of 8)

Table 2.14.3. (cont.) Reference Materials analysed for Pd. Certified, indicative and found value are expressed in µg L^{-1}

RM Certified or indicative value	Method	Instrumental technique	Found value	References
	Acid dissolution	ICP-SFMS	267 ± 40	Kollensperger et al. 2000
		ICP-MS	242 (Te-coprec.)	Morton et al. 2001
		HPIC-ICP-SFMS	226 ± 22	Hann et al. 2001
			224 ± 219	Hann et al. 2001
WMG-1 382±13	NiS-FA	ICP-MS	406 ± 9,2 Te-coprec.)	Zhou et al. 2001
		ICP-MS	394.8 ± 11.0 Te-coprec.)	Oguri et al. 1999
		LA-ICP-MS	416 ± 30	Figueiredo et al. 2000
		INAA	319 ± 53	Figueiredo et al. 2000
WMG-1 382±13	Pb-FA	ICP-MS	371 ± 18 Lab1; 396 ± 15 Lab2	Hall and Pelchat, 1994
CW-7 4.0 ± 1.3	Acid dissolution and Te coprecipitation	ICP-MS	6.7 ± 2.1 (external calibrat.) 4.3 ± 0.2 (isotopic dilution)	Gomez et al. 2003
CW-8 5.5 ± 1.8	Acid dissolution	ICP-MS (Te coprecipitation)	5.5 ± 1.2 (external calibrat.) 5.1 ± 0.7 (isotopic dilution)	Gomez et al. 2003
		ICP-MS(SF) ion exchange	6 ± 2 (below QL)	Hann et al. 2001
	Acid dissolution and separation and concentration with polyacrolein-isonicotinic acid hydrazone resin	ICP-MS	8	Ge et al. 2004
TDB-1 22.4±1.4	NiS-FA	ICP-MS	24.2 ± 1.8 (Te-coprec.)	Zhou et al. 2001
		GFAAS	21.2 ± 4	Zereini et al. 1997
	Pb-FA	ICP-MS	23.16 ± 1.24 Lab1; 23.35 ± 0.76 Lab2	Hall and Pelchat, 1994

(Part 5 of 8)

Table 2.14.3. (cont.) Reference Materials analysed for Pd. Certified, indicative and found value are expressed in µg L^{-1}

RM Certified or indicative value	Method	Instrumental technique	Found value	References
	Acid dissolution	ICP-MS (ID)	23.0 ± 2.99	Meisel et al. 2001
DZE-1 5	Acid dissolution	GFAAS	5 (Te-coprecipitation)	Sen Gupta , 1989
DZE-2 2	Acid dissolution	GFAAS	5 (Te-coprecipitation)	Sen Gupta , 1989
W-1 14 ± 3	Acid dissolution	GFAAS	11	Sen Gupta , 1989
W-1 14 ± 3	Alkaline fusion	RNAA	13 ± 0.2 17.7 ± 0.4	Stone and Crocket, 1993 Ahmad et al. 1977
CHR-BKg 70	Acid dissolution	ICP-MS (ID)	56.1 ± 7.29	Meisel et al. 2001
	NiS-FA	ICP-MS	55 ± 9	Juvonen et al. 1994
MINTEK 2/77 1670	NiS-FA	LA-ICP-MS	1720 ± 80	Jarvis et al. 1995
		ICP-MS	1449.7 ± 111.6 (Te-coprec.)	Oguri et al. 1999
CHR-Pt+ 80800	NiS-FA	LA-ICP-MS	78500 ± 1550	Jarvis et al. 1995
		ICP-MS	82200 ± 3000	Juvonen et al. 1994
DTS-1	Acid dissolution	GFAAS	18 (Te-coprecipitation)	Sen Gupta , 1989
	Alkaline fusion	NAA	2.6 ± 0.1	Ahmad et al. 1977
DTS-1 PCC-1 5.0-6.2	Acid dissolution	GFAAS	18 (Te-coprecipitation)	Sen Gupta , 1989
	Acid dissolution	NAA	9.0 ± 1	Bem and Ryan, 1985
	Alkaline fusion	NAA	6.3 ± 0.4	Ahmad et al. 1977
	Acid dissolution	GFAAS	(Te-coprecipitation)	Sen Gupta., 1989

(Part 6 of 8)

Table 2.14.3. (cont.) Reference Materials analysed for Pd. Certified, indicative and found value are expressed in μg L^{-1}

RM Certified or indicative value	Method	Instrumental technique	Found value	References
AGV-1 WGB-1 13.9 ± 2.1	Pb-FS	ICP-MS	11.73 ± 2.40 Lab1; 12.03 ± 1.75 Lab2	Hall and Pelchat, 1994
	Acid dissolution	ICP-MS (ID)	11.7 ± 1.40	Meisel et al. 2001
		ICP-MS (ID)	8.0 ± 0.7 (+ HF digestion)	Muller and Heumann, 2000
		ICP-MS (SF)	10.6 ± 2.7 (only AR)	
			11 ± 3 (ion-exchange)	Hann et al. 2001
WMS-1 1185 ± 44	Pb-FA	ICP-MS	1213 ±208 Lab1; 1362 ± 106 Lab2	Hall and Pelchat, 1994
NIST 2557	Acid dissolution	LA-ICP-MS	± 10% of certified value	Rauch et. al. 2001
		ICP-MS	Good agreement	
			246700 ± 11400 (proc.1)	Moldovan et al. 2002
			234700 ± 11100 (proc.2)	Moldovan et al. 1999
			246700 ± 11100	Gomez et al. 2000
		GDMS	234000 ± 4590 (for ^{105}Pd of one among five experiment)	Wayne, 1997
NIST 2556 326000± 1600	Acid dissolution	ICP-MS (multi-collector)	323900 ± 2900	Simpson et al. 2004
NIES 8	Acid dissolution	GFAAS	297 ± 56 (with column preconc.)	Boch et al. 2002
	Acid dissolution	ICP-MS	180 ± 28	Vlasankova et al. 1999
GPT-2 2.3 ± 0.2	NiS-FA	ICP-MS	2.4 ± 0.2	Li et al. 1998
GPT-4 60 ± 6	NiS-FA	ICP-MS	55 ± 2	Li et al. 1998
		LA-ICP-MS	92.5 ± 3.5	Figueiredo et al. 2000
		INAA	54 ± 24	Figueiredo et al. 2000

(Part 7 of 8)

Table 2.14.3. (cont.) Reference Materials analysed for Pd. Certified, indicative and found value are expressed in μg L^{-1}

RM Certified or indicative value	Method	Instrumental technique	Found value	References
GPT-6 568 ± 51	NiS-FA	LA-ICP-MS	586 ± 66	Figueiredo et al. 2000
		INAA	444 ± 50	Figueiredo et al. 2000
WITS-1 7.6	Carius tubes digestion	ICP-MS	5.59 ± 1.18	Pearson & Woodland, 2000
GXR-1 <0.1	Aqua regia	ICP-MS	181	Gowing and Potts, 1991
GXR-4 0.2	Aqua regia	ICP-MS	55	Gowing and Potts, 1991
NIST 1566 <2	Acid digestion	NAA	<2	Ben and Ryan, 1985
NIST 1573 <2	Acid digestion	NAA	<2	Ben and Ryan, 1985
NIST 1575 <2	Acid digestion	NAA	<2	Ben and Ryan, 1985

(Part 8 of 8)

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Tabel 2.14.4. Reference Materials used in Pd analysis. Producers and characteristics

RM	Matrix	Producer	Certified indicative values µg L^{-1}
PTC-1	Sulphide floatation	CANMET (n.a.)	12700 ± 700
PTM-1	Ni-Cu matter	CANMET (n.a.)	8100 ± 700
SARM-7*	Platinum ore	SABS	1530 ± 32
WPR-1 *	Altered peridotite	CANMET	235 ± 9
WMG-1 *	Mineral gabbro	CANMET	382 ± 13
WGB-1 *	Gabbro rock	CANMET	13.9 ± 2.1
WMS-1 *	Massive sulphide	CANMET	1185 ± 44
TDB-1 *	Diabase rock	CANMET	22.4 ± 1.4
UMT-1 *	Ultramafic ore tailings	CANMET	106 ± 3
MA-2a	Waste rock	CANMET (n.a.)	
SU-1a *	Ni-Cu-Co ore	CANMET	370 ± 30
2/77		SABS (n.a.)	1670
PTA-1	Platiniferous black sand	CANMET(Pt)	
TDB-1 *	Diabase rock	CANMET	22.4 ± 1.4
DTS-1	Dunite	USGS (n.a.)	
PCC-1	Peridotite	USGS (n.a.)	5-6
WITS -1	Not mineralized silicified komatiide;	Cape Town S. Africa Univerity	7.9 ± 0.9
CW7**	Road dust	IRMM	4.0 ± 1.3
CW8**	Road dust	IRMM	5.5 ± 1.8
GPT-2	Stream sediment	GBW	2.3 ± 0.2
GPT-4	Ultrabasic rock	GBW	60 ± 9
GPT-6		GBW	568 ± 51
GBW07101	Ultrabasic rock	XIGMR	5
GBW07102	Ultrabasic rock	XIGMR	2
NMB 6a	Mafic rock, Stillwater		450 (n.t.)§§

(Part 1 of 2)

Tabel 2.14.4. (cont.) Reference Materials used in Pd analysis. Producers and characteristics

RM	Matrix	Producer	Certified indicative values μg L^{-1}
CHR-Pt+	Chromitite		80800
CHR-BKg	Chromitite		70 (proposed)
BCR-723	Road dust	IRMM	6.0 ± 1.8
NIST 2557	Recycled Monolith	NIST	233200 ± 1900
NIST 2556	Recycled Pellet (autocatalyst)	NIST	326000 ± 1600
NIST 2670	Urine	NIST (n.a.)	
NIST 1566	Oyster tissue	NIST	<2
NIST 1573	Tomato leaves	NIST	<2
NIST 1575	Pine needles	NIST	<2
JSD-2	Stream sediment	GSJ	21.2
IMEP-11	Auto catalyst	IRMM	
GXR-1	Jasperoid soil		<0,1
GXR-4	Copper mill-head		0.2
NIES 8	Vehicle exhaust particulates	NIES	
W-1	Diabase	USGS (n.a.)	14 ± 3
AGV-1	Andesite	USGS (n.a.)	0.92-2.5

(Part 2 of 2)

n.a.:Not Available;
* CRM for Pd; ** CWB7 is a test material used for preliminary interlaboratory study before BCR certification; CW8 stands for BCR 723;
n.t: Not Certified; CANMET: Canada Centre for Minera and Energy Technology; SABS: South African Bureau of Standards; GSJ: Japan Geol. Survey; NIES:National Institute for Environmental Studies, Japan; USGS: U.S. Geological Survey; GBW: National Research Centre for Certified Reference Materials, China; NIST: National Institute of Standard and Technology; XIGMR: Xian Institue of Geology and Mineral Resources, Chinese Academe; IRMM: Institute for Reference Materials and Measurements, Geel, Belgium

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3 Occurrence, Chemical Behaviour and Fate of Palladium in the Environment

Among other topics, the distribution and concentration of Pd in soils, waste water, snow, sewage sludge, sediments and air are discussed in this chapter. As shown by Bencs et al. (Section 3.11), elevated Pd concentrations occur in environmental media in close proximity to streets. In Section 3.6, Moldovan et al. demonstrate that Pd is present in higher concentrations compared to Rh and Pt in a mountain ecosystem (Aspe Valley, Pyrenees, France). Elevated Pd levels have even been found in polar and alpine snow (Boutron & Barabente, Section 3.5). This latter contribution discusses how Pd concentrations in recent snow are significantly higher than that measured in ancient ice. This indicates a widespread atmospheric contamination of Pd in the Northern hemisphere (Rauch et al. Section 3.1).

Increases in Pd concentrations can be attributed to the use of Pd-containing catalytic converters, since their introduction in 1993. The continued use of this metal in autocatalysts may have important environmental implications in the future. The potential toxic effects of Pd in living organisms are still being discussed (Moldovan et al. Section 3.6).

Elevated amounts of PGE not only occur in the direct vicinity of roads where they are emitted. These metals are also transported though wind and rain (Rauch et al., Section 3.1, 3.9). Platinum group element deposits on streets are washed away by rain, where they inevitably end up in treatment plants via sewage canals (Rauch et al., Section 3.1). Sewage treatment plants also receive waste water from other potential Pd sources such as private households, industry and hospitals (Schwesig et al., Section 3.2, Stüben & Kupper, Section 3.3). In addition to automobile catalytic converters, industries such as the dental, jewellery and chemical industries are important contributors to increased levels of Pd in sewage sludge (Stüben & Kupper 3.3).

Palladium concentrations in fluvial sediments and airbourne particulate matter have also been the focus of investigation (De Vos et al., Section 3.4, Zereini et al., Section 3.8). Palladium levels in airdust are a particularly important topic of study given the potential for this metal to elicit toxic responses upon inhalation. The biological effects of ultrafine Pd-containing particles are not yet fully known.

Zereini et al. investigated the distribution and concentration of Pd in both fractionated and total airborne particulate matter in samples collected in Frankfurt am Main, Germany. Their results show that the highest amounts occur in the direct vicinity of major roads. Concentrations were lower at the side street. Samples from the rural location contained the least amount of Pd. The concentration of Pd in samples collected at the main street sampling site in Frankfurt was 14.7 pg/m^3 and ranged between < 0.6 and 44.3 pg/m^3. This compares to samples collected in Salzburg in 2001, which contained an average Pd concentration of 16.5 pg/m^3 (Limbeck, Section 3.7). Palladium concentrations ranged from 7.1 to 31.2 pg/m^3 in this study.

As discussed by Parry & Jarvis in Section 3.10, the mobility and solubility of Pd in the environment are important factors in terms of its bioavailability. They show that Pd deposited on roads and roadsides is more mobile than Rh or Pt. As a result, greater amounts of Pd are taken up by plants and aquatic organisms. Angelone et al. (Section 3.12) conclude this chapter with a review of Pd in environmental media.

Zereini & Alt (Editors)

3.1 Regional and Global Transport of Platinum Group Elements from Automobile Catalysts

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Automobile exhaust catalysts were introduced in the US in the mid-1970s to reduce traffic-derived air pollution in urban areas, and have resulted in significant air quality improvements. It has however been demonstrated that a small amount of platinum group elements, the main active components in catalysts, are emitted during vehicle operation (Konig et al., 1992; Palacios et al., 2000; Moldovan et al., 2002) resulting in elevated concentrations of these normally rare metals in the urban and roadside environment (Gomez et al., 2002). While these metals were believed to remain in the urban and roadside environment, recent studies have suggested the possibility for regional and global dispersion of these elements.

A 2-year project with the co-authors as partners and funded by the Alliance for Global Sustainability was initiated in 2002 to provide a further understanding of PGE transport from roadside environments. This paper presents literature and project-related information on potential regional and long range transport, from automobile catalysts to global distribution.

3.1.1 PGE emission and atmospheric occurrence

PGE emission into the urban environment has been documented by both the depletion of PGE on the surface of catalysts (Moldovan et al., 2003), the occurrence of PGE in automobile exhaust fumes (Palacios et al., 2000; Moldovan et al., 2002) and elevated PGE concentrations in samples collected in the roadside environment (Alt et al., 1993; Zereini et al., 1997; Rauch et al., 2001; Gomez et al., 2003; Kanitsar et al., 2003; Kylander et al., 2003; Zereini et al., 2004).

PGE are principally emitted as particles, and airborne particles are therefore an important environmental compartment for PGE. Concentrations in the pg m^{-3} range have been reported in urban and roadside air (Alt et al., 1993; Petrucci et al., 2000; Gomez et al., 2001; Rauch et al., 2001; Gomez et al., 2002; Kanitsar et al., 2003; Zereini et al., 2004). Particle size is a key determinant for the atmospheric residence time of particles and knowledge of size distribution is therefore a key to understanding the environmental pathways of PGE. Large particles typically deposit close to their source, so large PGE-containing particles are expected to remain in the roadside environment. In contrast, small particles have a longer atmospheric residence time, so emission of small particles could lead to a widespread contamination. Particles with diameters of =5 mm can be transported over long distances and have been shown to reach polar regions (Delmonte et al., 2003). Small particles also present a greater health risk owing to their deeper penetration into the lungs, and may be more reactive in PGE transformations owing to their larger surface area.

A number of processes have been held responsible for the emission of PGE from catalysts (Palacios et al., 2000; Moldovan et al., 2002; Moldovan et al., 2003), including mechanical abrasion that would result in the emission of particles with diameters of several micrometer to the emission of single atoms by small crystallites (Palacios et al., 2000). The size of PGE-containing particles is expected to range from sub-micrometer to several micrometers. The particle size of PGE in urban air has been reported to range from 0.1 mm to 63.5 mm (Alt et al., 1993; Petrucci et al., 2000; Gomez et al., 2001; Rauch, 2001; Gomez et al., 2002; Kanitsar et al., 2003; Tsuzaki et al., 2003; Zereini et al., 2004).

Further characterisation of PGE containing particles has been obtained by a combination of surface analysis analytical techniques, including electron probe micro-analysis (EPMA), scanning electron microscopy (SEM), wavelength dispersive spectrometry (WDS) and time of flight-secondary ion-mass spectrometry (ToF-SIMS) (Tsuzaki et al., 2003). PGE containing particles with diameter in the range of 1-10 μm were identified in both automobile exhaust and urban air, although relatively few particles could be detected in atmospheric samples owing to a relatively low particle number. PGE concentrations (sum of Pt, Pd and Rh concentrations) in individual particles in automobile exhaust ranged from 0.23% to 61.7% (weight) with PGE occurring either individually or as a combination, and generally together with both Al and Ce, two major catalyst components. Both the wide variety of particle compositions and differences in physical appearance observed by SEM supports the occurrence of different types of particles and emission mechanisms.

Particle size distribution suggests that platinum group elements can be transported beyond the roadside environment by atmospheric transport. While sharply decreasing PGE concentrations with increasing distance from traffic (Schafer et al., 1998) has provided support for a relatively local contamination, widespread PGE dispersion would result in low concentration owing to the larger deposition area, although the total flux may not be negligible. Transport of deposited PGE in stormwater may result in further dispersion of these elements.

3.1.2 Regional transport

Regional transport of PGE from automobile catalysts is expected to have two main pathways; (1) atmospheric transport of emitted particles and (2) transport of deposited particles in stormwater. Atmospheric PGE transport was investigated by the study of PGE deposition in a high-altitude Alpine glacier (Monte Rosa Massif, Swiss-Italian Alps, Barbante et al., 2004) and an ombrotrophic peat bog (Thoreau's Bog, Concord, Massachusetts, USA, Rauch et al., 2004b). Stormwater transport was investigated by comparison of deposition in Thoreau's Bog with deposition in an urban lake (Upper Mystic Lake, Winchester, Massachusetts, USA, Rauch et al., 2004a), which receives both atmospheric and stormwater-derived metal inputs. Both the lake and the bog are located in western Massachusetts, USA.

A clear increase in Pt concentration was measured in ice cores from the Monte Rosa Massif following the introduction of catalysts in the mid-1980s in Europe. In contrast, Pd and Rh concentrations did not follow a similar trend, but were elevated throughout the 20th century. Increase of Pt concentration following the introduction of catalysts indicates that PGE emitted from catalysts can be transported on a regional scale, but elevated Pd and Rh concentrations before the introduction of catalysts suggest non-catalyst sources of these metals.

A further study of regional atmospheric transport was performed at Thoreau's Bog, a peat bog receiving minerals through atmospheric deposition only (Rauch et al., 2004b). Platinum, Pd and Rh were found to be enriched 694, 191 and 496 fold, respectively, compared with expected lithogenic PGE deposition, owing to predominantly anthropogenic sources. Automobile catalysts are the only known source of PGE in the vicinity of the bog (300 m from the closest road) and the results therefore indicate regional transport of PGE from the catalysts.

PGE concentrations in sediments from an urban lake were also found to have increased following the introduction of catalysts in 1975. Concentrations reached a plateau in the 1990s, with concentrations 6-16 times higher than pre-catalyst concentration, likely owing to the stabilization of the number of cars equipped with catalysts and improving catalyst technology (Fig. 3.1.1) (Rauch et al., 2003; Rauch et al., 2004a).

A comparison of deposition rates in the bog and the lake provides further understanding of PGE transport at a regional scale (Table 3.1.1). The higher deposition rate in lake sediments indicates that stormwater runoff is an important pathway of regional PGE transport. However, given that the watershed of Upper Mystic Lake covers 67 km^2, an even larger than observed deposition rate would be expected if all PGE deposited in the watershed (estimated from atmospheric deposition at Thoreau's Bog) were transported to and deposited in the lake. It follows that a large amount of deposited PGE remains in, or is exported from the watershed.

Elevated Pt and Pd concentrations, found in Boston Harbor downstream from Upper Mystic Lake (Tuit et al., 2000), are suggestive of PGE export from the watershed. However, the relatively high deposition rates in Boston Harbour are likely the result of additional sources in Boston, such as high traffic areas, sewage overflow and hospitals.

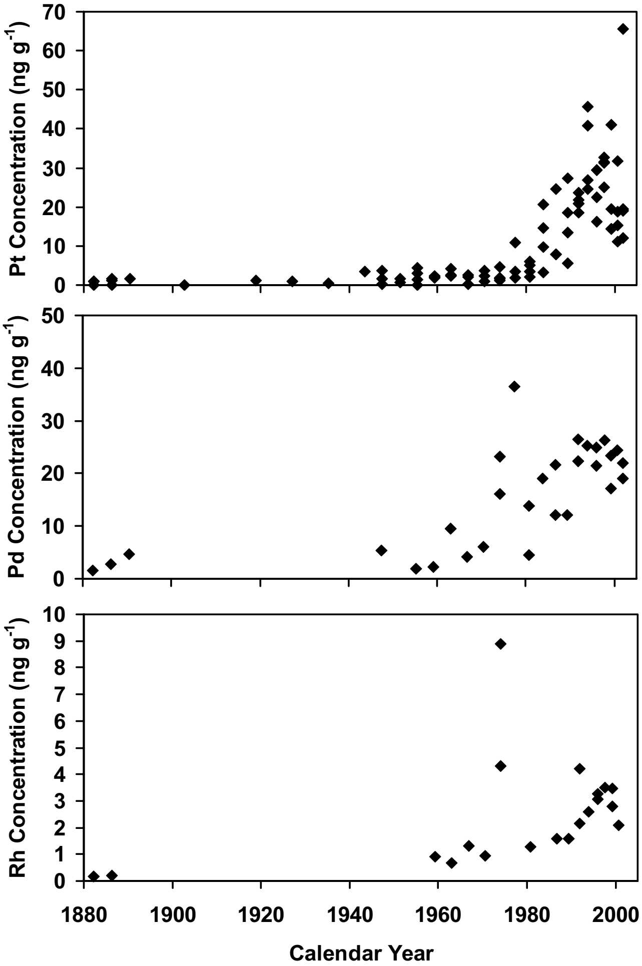

Fig. 3.1.1. Platinum, Pd and Rh concentration changes in Upper Mystic Lake sediments. Adapted from (Rauch et al., 2004a), reprinted with permission. Copyright 2004. American Chemical Society. Dating based on ^{210}Pb and independent markers

3.1.3 Global dispersion

Elevated PGE concentrations have been measured in recently deposited Greenland ice and snow (Fig. 3.1.2) (Barbante et al., 2001; Barbante et al., 2003). The absence of local sources provides evidence for long-range transport, although the sources and pathways are still largely unknown. Potentials sources include smelting activities in north-west Russia and

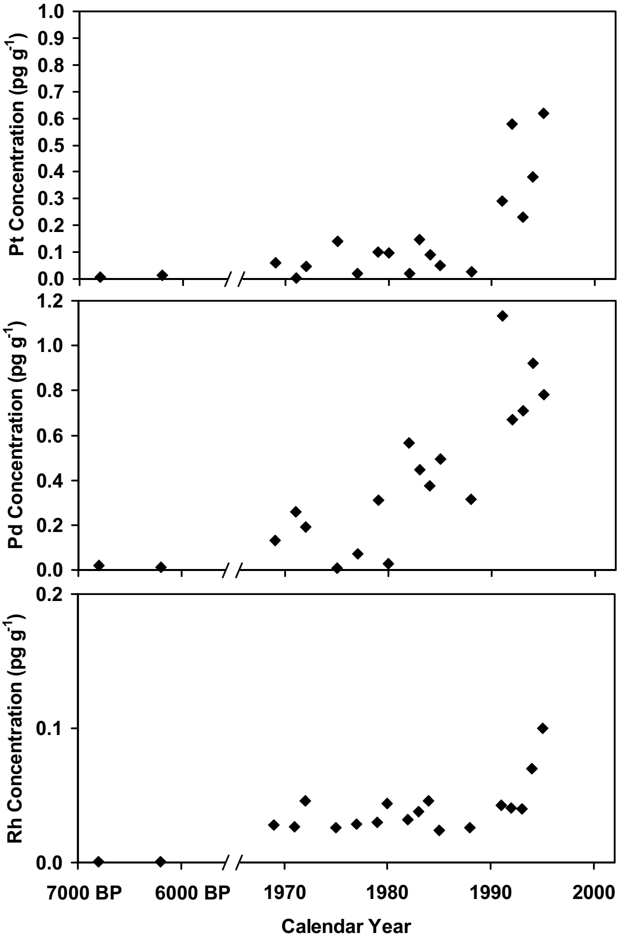

Fig. 3.1.2. Platinum, Pd and Rh concentration changes in Central Greenland ice and snow. Adapted from (Barbante et al., 2001), reprinted with permission. Copyright 2001. American Chemical Society

automobile catalysts. Emissions from industrial processes using PGE are likely to be relatively limited due to their high price and interest in minimizing PGE loss.

Higher PGE concentrations in 1969-1975 (prior to the introduction of automobile catalysts) than in ancient ice indicated the occurrence of non-catalyst PGE sources and long-range transport from these sources. Further increase following the introduction of automobile catalysts in 1975 may be

Table 3.1.1. Flux of PGE to Upper Mystic Lake sediments (Rauch et al., 2004a) and Thoreau's Bog (Rauch et al., 2004b). Lithogenic flux component for the Thoreau's Bog estimated using Al concentrations (Rauch et al., 2004b) and composition of the Upper Continental Crust (Wedepohl, 1995; Peucker-Ehrenbrink and Jahn, 2001)

Element	PGE flux (µg m^{-2} $year^{-1}$)			
	Upper Mystic Lake (average)		Thoreau's Bog (median)	
	1948-1971	1975-2002	Lithogenic flux	1979-2002
Pt	0.6±0.3	7±5	0.012	-
Pd	1.2±0.6	9±5	0.0035	0.68
Rh	0.22±0.06	1.1±0.5	0.0004	0.21

attributed to these devices. An automobile catalyst source is supported by the occurrence of PGE in particles <5 µm, a Pt/Rh concentration ratio similar to that in catalysts and aforementioned regional transport pathways. However, PGE concentration trends do not provide clear support for an automobile catalyst source; while Pd steadily increased after the introduction of catalysts, an increase in Pt and Rh concentrations was not observed until the 1990s (Fig. 3.1.2).

A further identification of the sources of PGE in Central Greenland was attempted using a high resolution record of PGE concentration in 1991-1995 snow (Barbante et al., 2003). Elevated Pt concentrations in 1991-1992 snow have been attributed to an increase in Pt production in Russia. There is however no direct relationship between concentrations in snow and Russian production. In addition, a similar increase in Pd production was not seen in Greenland snow.

The sources and pathways of PGE in Central Greenland are still largely unknown. Concentration profiles indicate that there is no clear relationship between potential sources and deposition. This is likely the result of the occurrence of multiple sources, combined with meteorological factors that affect transport of particles from lower latitudes to Greenland. Potential sources which have been identified include automobile catalysts and Russian smelters.

3.1.4 Spreading of the source

In addition to regional and potential long-range transport, the global distribution of PGE in the environment is characterised by the distribution of their sources. Automobile catalysts were first introduced in the US in 1975 as a remedy for air pollution in urban areas. Catalysts have since then been introduced in many countries worldwide. While developed countries were the firsts to adopt automobile catalyst legislation, catalysts have recently been mandated in developing countries in an attempt to tackle air quality issues in rapidly growing urban areas, such as in India, China and Brazil. In addition, the importation of cars from Europe, the US and Japan has also resulted in the introduction of catalysts in countries where catalysts are not mandatory (Kylander et al., 2003).

The global distribution of catalysts is therefore expected to change in coming years; in particular, the number of catalysts in the Southern Hemisphere will certainly increase in coming years. The use of catalyst equipped cars in developing countries also raises concern over the effect of poor vehicle maintenance on PGE emission as engine malfunction could result in higher emission rates (Helmers, 1997).

3.1.5 Conclusion

While it has now been demonstrated that PGE are emitted from automobile catalysts, the spatial extent of PGE contamination is still poorly known. Recent results provide evidence than PGE can be transported from the roadside environment, possibly due to their occurrence in fine particles and stormwater runoff. Regional atmospheric transport has been documented. PGE deposited near roads can be transported to aquatic environments during rain events, resulting in contamination of receiving waters and transport to coastal environments. Long-range transport of PGE from automobile catalysts has not been demonstrated, but knowledge of PGE particle size distribution, the possibility of regional transport and increasing concentrations in Greenland snow and ice provide strong indication for widespread contamination. Other, yet unidentified, sources of PGE are also likely to contribute to the global PGE load.

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3.2 Palladium in Waste Waters and Surface Waters of North Rhine-Westfalia

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3.2.1 Introduction

Increasing concentrations of platinum group elements (PGE) in several environmental compartments have been reported in a number of recent publications (Helmers et a. 1998, Kümmerer 1999, Laschka & Nachtwey 1997, Pyrzynska 2000, Schäfer et al. 1999, Sures et al. 2002a,b). Abundant data on platinum in the environment are available, but there are still important gaps of knowledge concerning the main sources, pathways and sinks of palladium (Pd) in the environment. This is mainly due to the difficulties in the reliable analysis of trace amounts of Pd in real samples, which is hampered by a number of severe interferences. The use of Pd in autocatalysts, dental alloys, electronics and as a catalyst for numerous industrial applications are supposed to be the main sources for Pd in the environment. For the near future, a further increase of the global palladium demand is forecast (Kendall 2004), and thus increasing emissions of palladium into the environment can be expected.

Increasing contents of Pd have been reported from sewage sludge (Schäfer et al. 1999), and recent investigations on biota have shown that aquatic organisms can accumulate Pd very effectively (Sures et al. 2002b). Thus, Pd input to surface waters by industrial effluents and other waste water sources may be an important link in the biogeochemical cycle of Pd. At present, concentrations of palladium in aquatic systems are usually far below the acutely toxic level. However, long-term effects of Pd-bioaccumulation and its impact on aquatic ecosystems and man as the final link of the foodweb cannot be evalutated with the limited data available today. Pd input from diffuse sources and point sources like road wash-off, sewage treatment plants, and industrial emittents are likely to be significant sources of Pd in surface waters, but little is known about the quantitative relevance of these pathways. Furthermore, only limited data about the level of contamination of surface waters are available. Therefore, the objectives of this study were (i) to investigate the current level of contamination of surface waters with Pd, (ii) to find out relevant sources for Pd in aquatic systems, and (iii) to estimate the Pd fluxes these sources account for.

3.2.2 Material and Methods

Site

The investigations were carried out in North Rhine-Westfalia (NRW), a federal state in the western part of Germany. The population is approximately 17 million people which is ~ 21% of the total population of the Federal Republic of Germany. Especially the area between the rivers Rhein, Ruhr and Emscher is a congested urban area characterized by a high degree of industrialisation and high population density. The core of this area, the so-called „Ruhrgebiet“, was dominated by coal mining activities in the past, and has now evolved into a modern megalopolis with a multifaceted structure of diverse commercial and industrial activities.

Strategy

To identify and quantify the most important pathways of palladium into surface waters, the following strategy was applied:

- preliminary measurements (screening) of a number of municipal and industrial wastewaters
- subsequent monitoring of selected sampling locations with elevated Pd-concentrations
- calculation of Pd fluxes from the investigated sources

Analytical methods

Determination of palladium in waste waters is hampered by a number of interferences. Analysis by inductively coupled plasma – mass spectrometry (ICP-MS) is a very sensitive analytical tool suitable for trace and ultratrace analysis of most metals. However, quantification of Pd by ICP-MS is prone to severe interferences by polyatomic molecules of other elements (e.g. by SrOH, MoO, YO, ArCu, ZrO). In surface waters, and especially in waste waters, the concentration of some of these elements exceed the Pd concentration by several orders of magnitude (up to a factor of 10^6).

The only way to cope with these difficulties and to enable a reliable Pd analysis in environmental samples is a careful matrix separation and/or a selective preconcentration of the analyte.

Table 3.2.1. Instrumental parameter settings for analysis of Pd by ICP-MS

Parameter	Value
Plasma power	1250 W
Gas fluxes:	
Plasma gas	15 l min^{-1}
Auxiliary gas	0.9 l min^{-1}
Nebulizer gas	0.90 – 1.05 l min^{-1}
Sample uptake	~ 1 ml min^{-1}
Wash step	90 s
Sample flush	90 s
Measurement mode	peak hopping
Dwell time	75-150 ms
Sweeps/Reading	30
Readings/Replicate	1
Replicates	3
Internal standards	^{115}In 1 µg l^{-1}
Analyte masses	^{104}Pd, ^{105}Pd, ^{106}Pd, ^{108}Pd, ^{110}Pd
Interferent masses	^{63}Cu, ^{65}Cu, ^{85}Rb, ^{86}Sr, ^{87}Sr, ^{88}Sr, ^{89}Y, ^{90}Zr, ^{98}Mo, ^{114}Cd

Analysis of waters and waste water samples was done with an Elan DRC II (PerkinElmer) after microwave digestion (with aqua regia) and subsequent cation exchange pretreatment (Dowex® 50 WX 8). Matrix separation by cation exchange is based on the fact that in aqueous solutions with sufficient chloride concentration (e.g. acidified by HCl) platinum group elements form anionic chlorocomplexes, whereas most of the relevant interfering elements are present as cationic species. In preliminary studies, this procedure had been tested with synthetic waste water samples containing up to 10^6-fold excess of interfering elements. In some cases, additionally to the cation exchange pretreatment, mathematical correction of interferences by daily correction factors (measured in solutions with defined concentrations of the relevant interfering elements) was necessary. Details on the use of cation exchange pretreatment and the application of mathematical corrections for analysis of Pd are given by Ely et al. (1999), Meisel et al. (2003) and Gomez et al. (2000). Instrumental parameter settings are given in Table 3.2.1.

The method was validated by measuring digests of the certified reference material BCR-723 (road dust). The instrumental detection limit of the Elan DRC II for measurement of ^{105}Pd is approximately 0.1 ng l^{-1}. Due to the high susceptibility of Pd measurements to interferences, this detection limit can seldom be achieved in real samples. Based on the repeated measurement of procedural blanks and standard solutions containing varying amounts of interferents, limit of detection and limit of quantitation were estimated to be 1 ng l^{-1} and 2 ng l^{-1}, respectively. Based on trueness and precision data of repeated measurements of the certified reference material BCR-723 a combined measurement uncertainty of 20% was calculated.

3.2.3 Results

Palladium in the river Rhine and its tributaries

On six sampling dates from October 2003 until July 2004 samples were drawn from the river Rhine and six tributaries (Sieg, Wupper, Lippe, Erft, Emscher, Ruhr). In all samples total Pd and dissolved Pd (after filtration < 0.45 µm) were analysed. In all cases the concentration of Pd was below 2 ng l^{-1}. Palladium content was also analyzed in selected samples of suspended particulate matter from the tributaries, and ranged from 2 to 18 ng g^{-1} (Table 3.2.2), with highest contents in suspended particulate matter from the rivers Emscher and Ruhr.

Table 3.2.2. Pd content of suspended particulate matter from the river Rhine and its tributaries

River	Site	Pd in ng g^{-1}
Rhine	Bad Honnef	3
Rhine	Düsseldorf	7
Rhine	Bimmen	5
Sieg	Menden	3
Erft	Eppinghoven	2
Ruhr	Duisburg	10
Emscher	Dinslaken	18

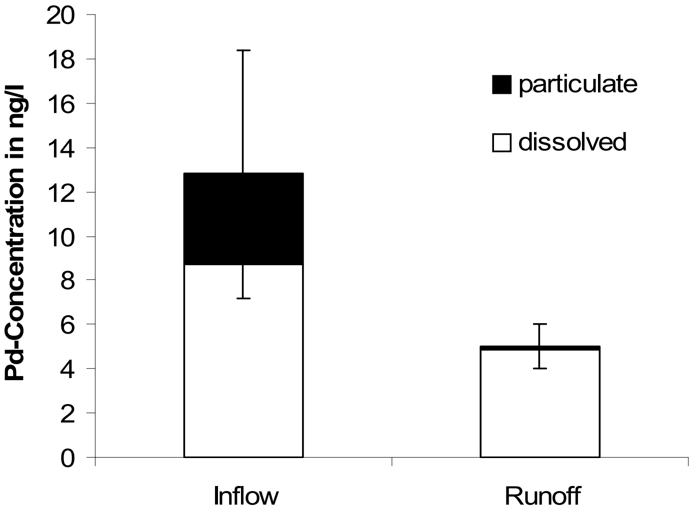

Fig. 3.2.1. Pd concentrations in inflow and runoff from rainwater basins for highway wash-off

Road wash-off from highways

For exploratory investigations, inflow and runoff from six rainwater retention basins for road washoff from three highways in NRW (A 3, A 40 and A 42) were sampled and analysed for total and dissolved concentrations of palladium.

Palladium concentrations were highly variable between the different rainwater basins. Inflow of palladium occurred at least partly bound to particles, wheras in the runoff, Pd concentrations were lower and nearly all Pd in the runoff was in the dissolved fraction (Fig. 3.2.1). Thus, approximately 50% of the Pd inflow was retained in the rainwater basins, probably by sedimentation of Pd bound to particles.

To enable mass balance calculations for traffic-borne Pd in road wash-off from highways, inflow and runoff from a rainwater basin at the highway A 3 were sampled on a regular basis from October 2003 until June 2004. Concentration of total Pd varied from < 2 ng l^{-1} to 58 ng l^{-1}. Calculation of total Pd fluxes was based on the assumption that evaporation and lateral flow from the road surface were negligible and 100% of the precipitation reached the rainwater basin. Annual fluxes of Pd (in μg m^{-2} a^{-1}) were calcu-

Table 3.2.3. Fluxes of total Pd from road wash-off from a highway in NRW

	Pd flux in µg m^{-2} a^{-1}	Pd flux in mg km^{-1} a^{-1}
Inflow	10	260
Runoff	6	165

lated by multiplying the mean Pd concentration (8 ng l^{-1}) by the precipitation amount (annual sum) of a nearby meteorological station. Fluxes were also normalized with respect to the road width to obtain fluxes per length unit of the highway in mg km^{-1} a^{-1} (Table 3.2.3).

To enable a comparability with other highways and to estimate the total Pd input from highways into surface waters of NRW, an immission factor for traffic-borne Pd input into surface waters was calculated according to the following equation (details on parameters see Table 3.2.4):

$$I = \frac{C \times N \times B}{365d \times D} \times 10^3 m\ km^{-1} \tag{1}$$

Using these data, the traffic-borne input of Pd to surface waters via road-washoff can be calculated to be **4 ng km^{-1}** for each vehicle.

Table 3.2.4. Estimate of traffic-borne input of total Pd to surface waters of NRW

Parameter	Description	Value	Unit	Data source
C	Annual mean Pd concentration in runoff	8	ng l^{-1}	this study
N	Long-term mean of annual precipitation at the investigated site	773	l m^{-2}	DWD (2004)
B	Road width	26	m	MVEL NRW (2002)
D	Traffic volume (number of vehicles)	110,00 0	d^{-1}	MVEL NRW (2002)
I	Immission factor for traffic-borne Pd input to surface waters	4	ng km^{-1}	this study

Based on Pd contents in soil, Abbas et al. (1998) have estimated considerably higher emission rates of traffic-borne Pd emission rates (15-24 ng km^{-1}), but it has to be considered that significant amounts of Pd emitted by car exhaust are either transported via the atmosphere or deposited onto soil in the immediate vicinity of the roads. Thus, it seems quite reasonable that only approximately one fourth to one sixth of the Pd emitted from autocatalysts is transported into the aquatic systems by road wash-off.

Based on the total length of highways in NRW (2,185 km) and the mean traffic volume on highways in NRW (58,300 d^{-1}) the annual input of traffic-borne Pd into surface waters via rainwater basins of highways can be calculated to be approximately 190 g a^{-1}.

For the following reasons, this can be regarded as representative for the total direct traffic-borne Pd input into surface waters of NRW via road wash-off:

- annual mileage on highways is 54% of the total mileage outside the cities in NRW
- in engine test bench experiments, a positive correlation between velocity and emission of PGE was identified. At velocities typical for highways, emission factors for PGE were up to tenfold higher than at velocities typical for urban traffic.
- wash-off from urban roads is not a direct input to surface waters, because in most cases it is discharged into the municipal waste water system. Thus, the urban input of traffic-borne Pd into surface waters is taken into account by investigating Pd fluxes in runoff from municipal sewage treatment plants (see below).

Industrial effluents – direct dischargers

To identify the relevant industrial sources for Pd, industrial effluents of various origin were sampled during 2003. Sampling sites were selected according to the following criteria:

- waste waters from industrial sectors where the use of platinum group elements is known, probable or at least possible, like
  chemical industry
  production of hydrocarbons
  production of glass and mineral fibres
  production of synthetic fibres, plastic foils, sponge cloth
  petrol industry
- waste waters from industrial sources that are known to have a high load of metals in general, e.g.
  steel production

cooling systems (from production of steel, petrol products, synthetic fibres)
nonferrous metals production
metal processing

- waste waters from handling, use or recycling of materials that are known to contain at least trace amounts of palladium (like electronic scrap, silicone products, geological materials)
  fluegas scrubbing from waste incineration and combustion plants
  landfill leachate

The waste water categories given above are defined by the German Waste Water Ordinance (AbwV 2002) for surveillance purposes. In a first step, 44 different industrial effluents were analysed for platinum group elements. In a second step, only sampling locations with concentrations of at least one PGE 5 ng/l were selected for a monitoring program (36 effluents from 10 industrial sectors).

At this sites, samples were drawn in different intervals, and Pd-fluxes were calculated from waste water fluxes and Pd concentrations. These investigations were restricted to direct dischargers (i.e. industrial effluents

Table 3.2.5. Estimate of sectoral emission of total Pd to surface waters by direct dischargers

Industrial sector	Pd flux by direct dischargers $g\ a^{-1}$
Briquette production	27
Ceramic products	0.1
Chemical industry	823
Cooling systems	11
Hydrocarbon production	13.3
Nonferrous metals production	1.6
Metal production production	4.5
Synthetic fibres production	165
Flue gas scrubbing	34.5
Landfill leachate	1.8
Total sum	1,082

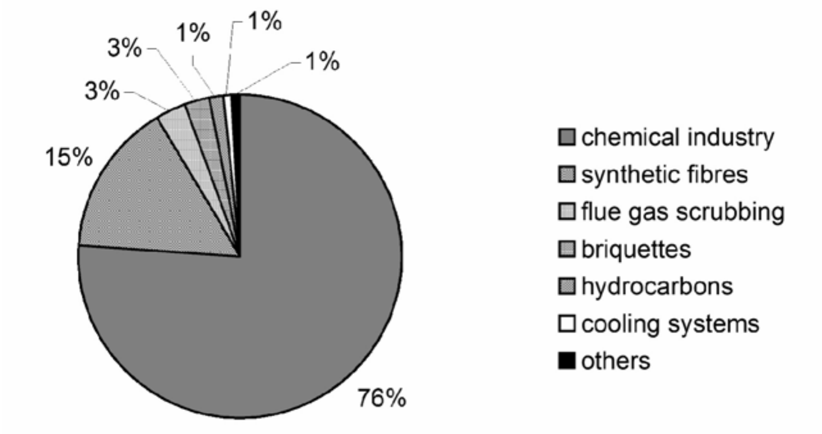

Fig. 3.2.2. Contribution of individual industrial sectors to the emission of total Palladium to surface waters in North Rhine-Westfalia by direct dischargers

that are discharged directly into the watercourse), because most of these dischargers are sampled on a regular basis as part of an official surveillance strategy by environmental agencies in NRW.

The Pd-fluxes by indirect dischargers (i.e. industrial effluents that are discharged into the municipal sewage system) are accounted for by accompanying measurements in effluent of numerous municipal sewage treatment plants (see below).

In most cases the concentration of dissolved Pd (filtration < 0.45 μm) ranged from < 2 ng l^{-1} to 10 ng l^{-1}, whereas concentrations of total Pd (after microwave digestion with aqua regia) were usually considerably higher, in some cases by more than one order of magnitude. Highest Pd concentrations (up to 180 ng l^{-1}) were detected in effluent from landfill leachate, flue gas scrubbing, chemical industry and metal processing.

From May 2003 until June 2004 up to six samples were drawn from each direct discharger and analyzed for total Pd concentrations. Total Pd fluxes by direct dischargers of each industrial sector were calculated as follows: multiplication of the total Pd concentration of each sampling date by the total annual waste water flux of the respective discharger, and calculation of an arithmetic mean of these separate estimates. These arithmetic means were added up for each industrial sector. Based on the ratio between the annual waste water flux of the investigated direct dischargers and the waste water discharge of all direct dischargers of the respective industrial sector, Pd fluxes were extrapolated to the Pd flux of all direct dischargers of the respective industrial sector (Table 3.2.5).

The emission of total Pd into surface waters by direct dischargers in North Rhine-Westfalia amounts to approximately 1.1 kg a^{-1} (Table 3.2.5). More than ¾ of the Palladium emission by direct dischargers comes from the chemical industry (Fig. 3.2.2.). Due to protection of anonymity it was not possible to obtain further information concerning the origin of the investigated effluents from the chemical industry. Production of synthetic fibres is responsible for 15% of direct Pd discharge via industrial effluents, followed by effluents from flue gas scrubbing and cooling systems (3% both).

3.2.4 Indirect dischargers

Dental offices

Dental offices are supposed to be a source of palladium to the sanitary sewer due to the dental vacuum systems that collect and discharge dental wastes during dental office procedures. More than 90% of the common dental alloys contain palladium in various amounts (Tschernitschek et al. 2001), and thus during all procedures where drilling or abrasive techniques are applied on dental alloys, a transport of Pd-containing particulate matter into the dental wastewater system is likely. However, quantification of Pd emission from dental offices in NRW was difficult because many dentists were reluctant to admit sampling of waste water from their amalgam separators. Nevertheless, in three dental offices supernatant of amalgam separators could be sampled and analyzed for concentrations of total palladium. In all cases sampling was performed in the morning prior to the first therapy to avoid current influx, and to enable comparable sedimentation conditions in the sampled separators. Pd concentration ranged from 170 to 251 ng l^{-1} (mean: 217 ng l^{-1}). As a first estimate, annual Pd emission from all dental offices in NRW was calculated according to the following equation (for details on parameters and assumptions see Table 3.2.6).

$$Q = A \times B \times C \times D \times E \times 10^{-6}\ \mathrm{g}\ \mu\mathrm{g}^{-1} \qquad (2)$$

Based on these calculations a total Pd amount of 55 g a^{-1} is emitted from dental offices in NRW. Compared to other Pd sources like industrial direct dischargers or road wash-off, this pathway is only of minor importance.

Table 3.2.6. Parameters used to estimate Pd-emission from dental offices

Parameter	Description	Value	Unit	Data source
A	number of dentists and orthodontists working in dental offices in NRW	9600		MFJFG 2001
B	average number of operating days per dentist	220	$d\ a^{-1}$	estimate[1)]
C	average daily operating time of a treatment unit with waste effluent system per dentist	4	$h\ d^{-1}$	estimate[1)]
D	average amount of waste effluent of a treatment unit	30	$l\ h^{-1}$	Daxbeck et al. 2000
E	mean concentration of total Pd in dental waste effluent	217	$\mu g\ l^{-1}$	this study
Q	annual Pd emission	55	$g\ a^{-1}$	this calculation

[1)] from interviews with dentists of the investigated offices

However, it has to be considered that this estimate is based on a very limited number of samplings, and needs to be confirmed by further investigations.

Recycling of autocatalysts

Autocatalysts contain up to several grammes of PGE. Prior to disposal of old cars, catalysts are usually removed and dismantled. During this process, the fragile ceramic monolith can burst and Pd-containing particles are scattered. Furthermore, scrap cars or removed catalysts are often cumulated and stored in open-air wasteyards prior to the recycling process. Precipitation on this areas leads to runoff, which is often discharged into the municipal canalisation.

To investigate this pathway, runoff from the premises of a scrap metal merchant specialised on the dismantling of autocatalysts was sampled and analysed for concentrations of Pd. The investigated company is equipped with a small sewage treatment plant consisting of a sedimentation tank and an oil separator. Samples were drawn at the outlet of the water treatment plant, where runoff is discharged into the municipal canalisation. Pd concentrations ranged from 328 ng l^{-1} to 5,000 ng l^{-1} (mean: 2,400 ng l^{-1}).

Based on precipitation data from nearby meteorological stations (800 mm a^{-1}) and a total area of 4500 m^2 of the investigated premise, a total annual Pd flux of 9 g a^{-1} can be calculated. As the number of companies dismantling autocatalysts in Northrhine-Westfalia is very small (2-5), the total Pd input from this sector is likely to be < 100 g a^{-1}.

Table 3.2.7. Concentrations and fluxes of total Pd in effluent from sewage treatment plants

Treatment plant[1)]	Annual water discharge m^3 a^{-1}	Total Pd concentration (mean) ng l^{-1}	Annual Pd flux by runoff g a^{-1}
01	3,000,000	< 2	< 5.9
02	1,500,000	< 2	< 3.1
03	3,000,000	< 2	< 5.9
04	3,000,000	< 2	< 6.4
05	6,000,000	< 2	< 12
06	2,000,000	< 2	< 3.6
07	150,000,000	< 2	< 396
08	50,000,000	< 2	< 96
09	4,000,000	< 2	< 8
10	400,000,000	2.4	1070
11	3,000,000	< 2	< 6.2
12	8,000,000	< 2	< 15
13	8,000,000	2	< 15
14	50,000	< 2	< 0.1
15	2,500,000	12	30
16	10,000,000	8.4	78
17	30,000	< 2	< 0.03
18	1,400,000	< 2	< 2.8
19	13,000,000	< 2	< 25
20	14,000,000	2	29
21	5,000,000	< 2	< 10
22	20,000,000	2	43
23	40,000,000	2.1	81
24	10,000,000	< 2	< 24

(Part 1 of 2)

Table 3.2.7. (cont.) Concentrations and fluxes of total Pd in effluent from sewage treatment plants

Treatment plant[1)]	Annual water discharge $m^3\ a^{-1}$	Total Pd concentration (mean) $ng\ l^{-1}$	Annual Pd flux by runoff $g\ a^{-1}$
25	10,000,000	2.2	22
26	2,000,000	< 2	< 4
27	5,000,000	4.3	21
28	7,000,000	< 2	< 14
29	40,000,000	2.3	94
30	8,000,000	< 2	< 15
31	200,000	< 2	< 0.4
32	8,000,000	< 2	< 15
33	2,000,000	3.2	6.3
Total	839,680,000		1,475

(Part 2 of 2)

1) Treatment plants were anonymized

Runoff from municipal sewage plants

In North Rhine-Westfalia, the majority of municipal sewage plants is operated by eleven water associations, which are responsible for designated river basins. Six of these water associations were involved in this study and provided effluent samples from 33 water treatment plants. Each water association selected three to ten treatment plants representative for the special pollution scenario of the respective river basin.

From July 2003 to June 2004 between one and 20 samples were drawn from each treatment plant. In total, 209 runoff samples from sewage treatment plants were investigated. Concentrations and fluxes of Pd in effluent from municipal sewage treatment plants are given in Table 3.2.7.

The annual Pd flux was calculated by multiplying the average concentration of total Pd in the runoff by the total annual water discharge of the treatment plant. The average concentration of each treatment plant had been calculated as arithmetic mean of Pd concentrations from single sampling events. For this calculation, concentrations below the quantitation limit (< 2 ng l^{-1}) were set to 50% of the quantitation limit (1 ng l^{-1}). If this was the case for more than 2/3 of the sampling events, only an upper limit for the Pd discharge of the respective treatment plant was calculated based on the quantitation limit. These plants were not included in the final summation of Pd fluxes.

In most treatment plants, concentrations of total Pd in the effluent were below the detection limit, and thus Pd fluxes could only be calculated for a limited number of plants. The total annual Pd flux from these plants amounts to approximately 1.5 kg a^{-1} (Table 3.2.7).

The total annual effluent flux of the 33 investigated treatment plants amounts to 839 x 10^6 m^3 a^{-1} which is approximately 26% of the total annual effluent flux from sewage treatment plants in North Rhine Westfalia (3,228 x 10^6 m^3 a^{-1} according to MUNLV 2003). Extrapolation to this total annual effluent flux leads to a palladium discharge from sewage treatment plants in the order of 5.7 kg a^{-1} in North Rhine-Westphalia.

3.2.5 Discussion

Concentrations of total and dissolved palladium in surface waters of North Rhine Westfalia were usually below quantitation limit (2 ng l^{-1}), but traces of Pd could be quantified in suspended particulate matter. This emphasizes the role of interactions with solid phases in case of Pd. Furthermore, in most investigated effluents, concentration of total Pd was considerably higher than concentration of dissolved Pd, and thus all flux calculations were based on concentrations of total Pd.

Municipal sewage treatment plants were identified as the main source for total Pd (5.7 kg a^{-1}). Minor contributions came from industrial direct dischargers (~ 1.1 kg a^{-1}) and wash-off from highways (~ 0.2 kg a^{-1}). In summary, this amounts to a Pd input to surface waters in NRW of approximately 7 kg a^{-1}.

The origin of palladium in effluent from sewage treatment plants could not be identified in this study. However, as road wash-off and waste water from dental offices and recycling companies turned out to be negligible (at least in terms of total fluxes), effluents from industrial indirect dischargers are most likely to be the source for Pd in municipal sewage treatment plants. This is supported by the following facts: (i) investigations of waste water from direct dischargers have shown that industrial effluents (especially from the chemical industry) are a significant source for Pd, and (ii) the number of industrial indirect dischargers is by orders of magnitude higher than the number of direct dischargers (615 vs. 50,738 in 2002, according to MUNLV 2002).

This is not reflected in the relation of Pd fluxes from treatment plants and direct dischargers. One reason for this discrepancy is that in waste water treatment plants Pd may be effectively eliminated by sedimentation and interaction with solid phases, e.g. sewage sludge particles.

It may be reasonable to suppose that in case of indirect dischargers the relative importance of the specific industrial sectors is similar as found for the direct dischargers. Thus, effluents from the chemical industry and from the production of synthetic fibres may also be the most relevant sources for Pd in municipal waste water treatment plants.

3.2.6 Conclusions

Industrial effluents are a source of palladium to surface waters in North Rhine-Westfalia, either by direct discharge or via effluent of waste water treatment plants. Other sources like traffic-borne Pd input via wash-off from highways, waste water from dental offices or recycling processes seem to be negligible, at least in terms of total fluxes. However, due to the limited data this needs to be confirmed by further investigations. Furthermore, elevated Pd concentrations in effluents from these sources may be of local importance at the point of discharge.

The total input of Pd to surface waters from the investigated sources is approximately 7 kg a^{-1}, and surface waters in North Rhine-Westfalia are currently not significantly contaminated with Palladium. Input of Pd into surface waters seems to occur mainly in particulate form.

As palladium in rivers seems to be closely associated with solid phases (e.g. suspended particulate matter), interactions at the water-sediment interface (remobilisation from sediments and sewage sludges) and intermittent transport during flood events should be important topics of future research. Furthermore, other pathways like atmospheric deposition of (e.g. traffic-borne) Pd should also be quantified in future studies.

Acknowledgements

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3.3 Anthropogenic Emission of Pd and Traffic-Related PGEs – Results Based on Monitoring with Sewage Sludge

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Abstract

Palladium and other precious metals such as platinum, and rhodium are emitted to the environment due to autocatalysts. Besides this, other emission sources such as dental alloys, cancer drugs, jewellery and petrochemistry amount extensively and are part of the total PGE contamination in sewage sludge. The amount of PGE related to automobile catalysts can be defined by the Pt/Rh ratio of 5 to 6 and by the Pt/Pd ratio of 0.8. Due to the various sources and the mixture of the contaminants the ratio gets changed considerably so that further trace metals are needed for source identification. The emission of Pd is increasing in the last years due to higher Pd consumption especially as substitute for Pt in converters.

Sewage sludge as matrix which generally accumulates human consumables was selected for this study. Sewage sludge samples of various waste water treatment plants (WWTPs) in Switzerland were analysed and can be grouped into three different types. Type A represents waste water from households of villages with a Pd/Pt ratio of up to 3.8 and type B a mixture of domestic waste water and street runoff of villages and small towns with varying Pd/Pt ratios. WWTPs of Type C receive a mixture of the sources mentioned above plus industrial waste water exhibiting a lowest Pd/Pt ratio of around 1 and a Pt/Rh ratio of up to around 20 reflecting industrial influx. For source identification further trace elements (Zr, Rb, Cd, Zn, Cu, Ni, Ti, Pb, Sb) were chosen and evaluated by cluster analyses. Seven different clusters could be identified underlining the Pd, Pt and Rh content as traffic induced.

3.3.1 Introduction

Palladium (named after the asteroid Pallas), having a melting point of 1552°C and a boiling point of 3140°C, was discovered in 1803 by Wollaston. Palladium occurs along with Pt and other metals of the PGE in placer deposits of Russia, South and North America, Ethiopia and Australia. It is also found associated with the nickel-copper deposits of South Africa and Ontario. Its separation from the platinum metals depends upon the type of ore in which it occurs. It is a steel white metal, does not tarnish in air, and is the least dense and lowest melting of the PGEs. The metal is used in dentistry, watchmaking and in making surgical instruments and electrical contacts. Total worldwide supply in 1999 and 2000 was 265 and 238 tonnes for Pd and 156 and 165 tonnes for Pt, respectively (Johnson, 2001). In the year 2000, 146,000 kg Pd was used by autocatalysts, 24,700 kg for dental use, 58,600 kg for electronics and 15,000 kg for others. The growing demand for Pd in Europe is largely in response to the introduction of the Euro Stage III legislation from January 2000, i.e. the Pd-rich catalysts can meet stricter emission limits for petrol-fuelled vehicles, resulting in a further diverging from Pt-based technology (Johnson, 2001). Besides the regulation of vehicular exhaust, Pt is also applied as a catalyst in various chemical lines, in electrotechnology, manufacture of measuring instruments, textile industry, jewellery production and medicine. Dental industry surgery uses a lot of alloys which represent thus a source contributing to around 80% Pd, and up to 18% Pt of the total emission.

Since the mid eighties catalytic converters have been introduced to European cars in order to reduce the emission of gaseous substances in engine exhaust detrimental to the environment (Palacios et al., 2000a; Ravindra et al., 2004). The three way catalyst that incorporates lambda probe regulation will reduce on its active platinum and palladium surface nitrogen oxides, carbon hydrogens, and carbon monoxide emissions by up to 90%. Mechanical abrasion and vibration of vehicles in motion release catalyst particles, among them Pd, Pt, and Rh (Hodge and Stallard, 1986; Schlögl et al., 1987; König et al., 1992; Artelt et al., 2000; Palacios et al., 2000b). Recently, Barbante et al. (2001) have roughly estimated that the annual worldwide Pt emission only from the automobile catalytic converters can be as high as 0.5-1.4 ton year^{-1}. Detailed studies conducted on the emission of PGE due to modern three way catalysts revealed a release of Pt of 270 ng Pt (Eckhardt and Schäfer, 1997) and of 250 ng Pd per automobile and km, respectively (Ravindra et al., 2004), calculated on the base of emitted particulates. PGEs released from cars accumulate in road sediments and are transported into the sewer system, waste water treatment plants (WWTPs) and rivers during rainfall. The road runoff of Pd in Stuttgart and Karlsruhe varies from 15 to 146 μg/kg (Schäfer et al., 1996), in San Diego it reaches 280 μg/kg (Hodge and Stallard, 1986). In tunnel dust of Japan 297 μg/kg Pd were measured (Helmers et al., 1998).

For modern societies, water is the most extensively used good of all consumables. Most contaminants except for the ones occurring in the gaseous phase end up in waste water. Within the WWTPs, they are accumulated in sewage sludge either in primary forms or in secondary transformed forms, a small part remains in the soluble phase in the water stream. In case sewage sludge is applied as fertilizer contaminants are introduced to agricultural surfaces and accumulate in the soil or/and is further transferred into the food chain via plants.

The SEA project (observation of the metabolism of the anthroposphere) was created to monitor specific contaminants and to determine their main sources which are: (i) private households, (ii) atmospheric deposition and emissions released from traffic entering the sewer system by surface runoff, (iii) industry and craft industry. The focus of this paper is on Pd and other PGE as well as inorganic compounds to trace the amount of automobile, household and industry contaminants and to evaluate the environmental impact.

3.3.2 Locations, samples and methods

Sixteen WWTPs among the monitoring network of SEA (Fig. 3.3.1), including three types of sites (A, B and C), were selected for the present study. Sites of type A comprise a rural catchment, no industrial activities, very few craft industry and a separate sewer system. Type B exhibits the same properties as type A but the catchment has a combined sewer system and some more craft industry is present. Sites of type C comprise a rather urban catchment, industry and craft industry in the connected communities and a combined sewer system. Table 3.3.1 summarizes the properties of the monitoring sites. Details of the WWTPs for the different sites are given in Kupper et al. (2004).

Sampling was conducted between February and May 2001. From sites A11, B14, B16, B25 and C4, samples collected in spring 1998 were included in the present study.

The sampling procedure was as follows: First, the sludge in the storage tank was homogenized with a stirring device. Samples were collected from the storage tank with a sampling bottle with flexible bottom and lid at several points from the rim or the bridge of the storage tank. The bottle was

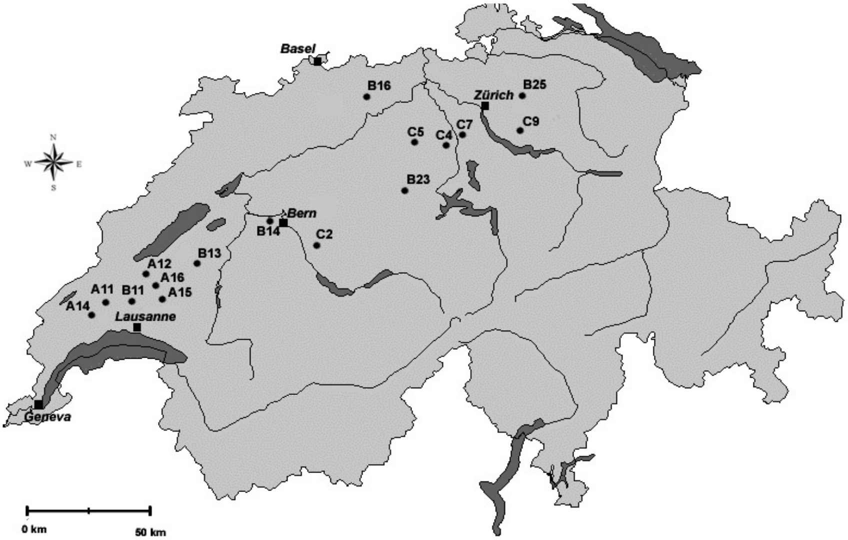


Fig. 3.3.1. Location of the monitoring sites of Switzerland

brought in at different depths in the sludge. Samples were obtained by closing the bottom and the lid of the bottle at the adequate position. Eight to 15 aliquots were collected in a container. The composite sample was cautiously homogenized before transferring the sample into glass jars. All sampling devices were of aluminium and were carefully rinsed with tap water before use.

The samples were dried at 105°C during approximately 24 h until steady state was obtained. The dry material was ground in a ball mill (particle size 0,5 mm) and stored in plastic containers.

Palladium, Rh and Pt contents in the 21 sewage sludge samples were analyzed by quadrupol ICP-MS (PlasmaQuad Turbo 2 plus, Fisons, UK). Prior to analysis, PGE contents in samples were preconcentrated and the matrix was separated by means of Ni-fire assay, following the method described in Schäfer et al. (1998). Fire assay was necessary not only to increase the element concentration but also to eliminate disturbing interferences from matrix elements. The isotopes ^{169}Tm and ^{209}Bi were used as internal standards to correct for fluctuations and drifts in signal intensity. Each reported ICP-MS result is the average of three individual runs, giving an instrumental precision generally better than 2% (1s). Accuracy was checked against an internal laboratory standard (ODP Basalt), used for quality control at the IMG since several years. Results on two standard aliquots processed in the same batch with the samples deviated to less than

10% from the average of many years. Detection limits, based on the threefold standard deviation of the blank values was found to be <0.05 µg/kg for Rh, 0.7 µg/kg for Pd and 0.3 µg/kg for Pt.

3.3.3 Cluster analysis

R-mode and Q-mode hierarchical cluster analysis, using the euclidic distances as similarity measure and Wards agglomeration method (e.g. Rock, 1988) as provided by STATISTICA V5.1 were applied to the major and trace elements and the PGE data of the sewage samples. To avoid scaling effects on the clustering results the data set was normalized as follows before applying cluster analysis:

$$Z_{ij}^{*} = (Z_{ij} - AVG_i)/s_i$$

with

Z_{ij} → value of element i in sample j
AVG_i → average of element i
s_i → standard deviation of element i

R-Mode clustering reveals similarities and dissimilarities in the behavior of the different elements within the sewage samples and allows for grouping the elements according to their associations and similar processes, e.g. geogenic, traffic related, organic processes, inorganic precipitation etc.

Q-mode clusters the samples based on their similarities and dissimilarities and thus allows for grouping according the sources of the sewage material.

3.3.4 Determination of the specific load

The release of a substance into the wastewater might be misinterpreted if concentrations in sewage sludge are considered only. High loads of organic matter from food processing industry result in a high sludge production of the treatment plant for example. This might dilute the concentration of the analyzed compound. The specific load in sewage sludge per inhabitant connected (capita) per year accounts for these effects and is thus a more reliable parameter. It is defined as follows:

$$L_{sp(i)} = C_{ss(i)} \times P_{ss} \times cap^{-1}$$

where $L_{sp(i)}$ is the load of the substance *i* in sewage sludge per inhabitant connected per year (mg cap^{-1} y^{-1}) (specific load), $C_{ss(i)}$ the concentration of the substance *i* in aerobically or anaerobically stabilised sewage sludge (µg/

kg dry matter, d.m.), P_{SS} the production of aerobically or anaerobically stabilised sewage sludge (1000 kg d.m. y^{-1}) and cap the number of inhabitants connected to the WWTP.

Table 3.3.1. Main characteristics of the monitoring sites and the corresponding wastewater treatment plants (2001).
Sewage: dom: domestic; sto: stormwater and infiltration water; ind: industrial
Wastewater treatment: EA: extended aeration; AS: activated sludge system
Sludge processing: AES: aerobic stabilisation; ANS: anaerobic stabilisation; H: hygienisation
* sequencing batch reactor instead of an aeration tank and a secondary clarifier
** trickling filter instead of an aeration tank

Site	Location	Connected inhabitants	Sludge production [kg d.m. y^{-1}]	dom	sto	ind	Wastewater treatment	Sludge processing
A11	Chevilly	210	2700	60	40	0	EA*	AES
A12	Cronay	284	3200	44	56	0	EA*	AES
A14	Sévery	989	26000	53	47	0	EA	AES
A15	Thierrens	514	12000	45	55	0	EA	AES
A16	Prahins	214	3500	88	12	0	EA	AES
B11	Echallens	5700	80’000	35	60	5	AS	ANS
B13	Cousset	1600	28’000	26	72	2	AS	ANS, H
B14	Wohlen	8460	155’000	27	73	0	AS	ANS
B16	Wenslingen	674	13’000	43	57	0	EA	AES
B23	Ruswil	3900	77’000	55	42	3	AS**	ANS
B25	Seuzach	6500	80’000	22	75	4	AS	ANS, H
C2	Konolfingen	7860	250’000	19	69	12	AS	ANS, H
C4	Muri	7800	175’000	24	62	14	AS	ANS, H
C5	Reinach	17’140	600’000	16	72	12	AS	ANS, H
C7	Affoltern	14’340	350’000	24	56	20	AS	ANS, H
C9	Gossau	11’300	220’000	33	58	11	AS	ANS

Table 3.3.2. Overview of the chemical composition of the different sewage sludge samples in mg/kg and µg/kg ash, respectively

Site	Location	Ignition loss	CaO	Fe_2O_3	Ba	Sr	Zr	Br	Pb	Cu	Zn	Cd	Sb	Rh	Pd	Pt	Pt/Rh	Pd/Pt
			wt.%						mg/kg						µg/kg			
A11	Chevilly '98	42.3	11.6	1.5	586	340	56	209	93	409	1925	3.4	0.0	2.7	28.8	15.7	5.84	1.84
A11	Chevilly	42.9	11.6	1.6	454	327	76	315	69	359	1653	5.4	<1.3	3.2	36.8	12.0	3.70	3.07
A12	Cronay	43.9	17.2	23.7	518	405	64	54	89	346	2276	4.0	3.6	4.4	25.1	6.6	1.49	3.82
A14	Sévery	50.0	7.2	12.1	213	132	24	139	25	151	438	0.0	<0.6	nd	nd	nd	nd	nd
A15	Thierrens	41.1	18.1	35.6	453	329	61	181	97	971	1720	3.0	2.6	3.4	23.1	10.6	3.08	2.19
A16*	Prahins	46.0	13.7	39.8	458	370	61	199	96	408	2064	3.6	7.2	3.3	47.5	32.9	9.84	1.44
B11	Echallens	57.3	19.6	14.8	1274	521	96	13	87	549	1835	3.6	5.3	5.6	53.1	14.3	2.54	3.70
B13	Cousset	58.1	14.6	13.3	897	431	77	22	55	275	949	2.2	1.7	3.7	30.5	12.2	3.31	2.50
B14	Wohlen '98	57.0	14.7	26.5	631	390	68	13	162	305	1341	0.0	4.0	4.8	25.5	25.8	5.31	0.99
B14	Wohlen	57.8	15.2	27.2	720	330	71	13	123	328	1257	0.6	7.1	16.0	24.5	44.9	2.80	0.55
B16	Wenslingen '98	36.6	13.9	29.6	1029	322	59	94	99	478	1315	3.9	0.0	1.8	17.1	11.7	6.68	1.46
B16	Wenslingen	32.8	16.9	24.2	1132	352	76	192	99	623	1452	5.1	2.4	3.5	36.3	15.1	4.25	2.41
B23	Ruswil	50.8	19.5	21.7	1259	605	70	31	82	442	1775	2.8	3.6	5.6	38.8	25.1	4.50	1.54
B25	Seuzach '98	56.4	20.6	21.5	1001	488	58	43	135	428	1603	4.2	0.0	2.7	46.4	17.9	6.54	2.60
B25	Seuzach	53.7	21.8	20.5	1294	532	91	82	133	566	1662	3.2	3.1	9.8	62.0	48.9	4.99	1.27
C2	Konolfingen	55.1	21.3	23.2	692	428	55	21	87	299	1239	2.1	2.0	3.6	33.0	69.5	19.24	0.47
C4	Muri '98	57.8	21.4	9.2	999	470	76	67	106	497	1338	1.9	0.0	2.7	13.7	11.9	4.47	1.15
C4	Muri	54.1	18.2	13.6	995	421	95	75	112	591	1492	2.3	5.7	7.1	41.8	39.7	5.60	1.05
C5	Reinach	53.0	17.8	10.1	705	443	65	54	274	405	1232	2.4	11.6	3.8	40.4	25.2	6.67	1.60
C7	Affoltern a. A.	55.9	23.0	15.9	924	472	1148	92	106	490	1616	1.5	8.6	6.3	52.6	37.2	5.95	1.41
C9	Gossau	48.3	23.8	26.2	806	485	58	61	78	415	1449	2.9	3.4	4.8	74.1	75.2	15.52	0.99

The sludge production provided by the personnel of the WWTPs was determined by registering the volume of aerobically or anaerobically stabilized sludge transported for use in agriculture or incineration and by the analysis of the dry matter content of each transported lot (Table 3.3.1).

3.3.5 Results and discussion

Twenty-one sewage sludge samples were analysed. The element contents of Pd and other PGEs and further trace metals are given in Table 3.3.2. A comparison of the PGE contents in various sewage sludge samples of different countries is given in Fig. 3.3.2. In Switzerland, the Pd content in sewage sludge was in general lower than 100 µg/kg (contents are given per kg ash unless otherwise stated). In the US, it was two orders of magnitude higher with Pd contents of more than 10,000 µg/kg (Furr et al. 1976). Extreme concentrations of Pt have been documented for sewage sludge of the city of Pforzheim of 1070 µg/kg d.m. reflecting the contamination of the jewellery industry and 2-58 µg/kg Pt d.m. of rural areas of south-east Germany (Laschka and Nachtwey 1997). In a detailed study, Lottermoser

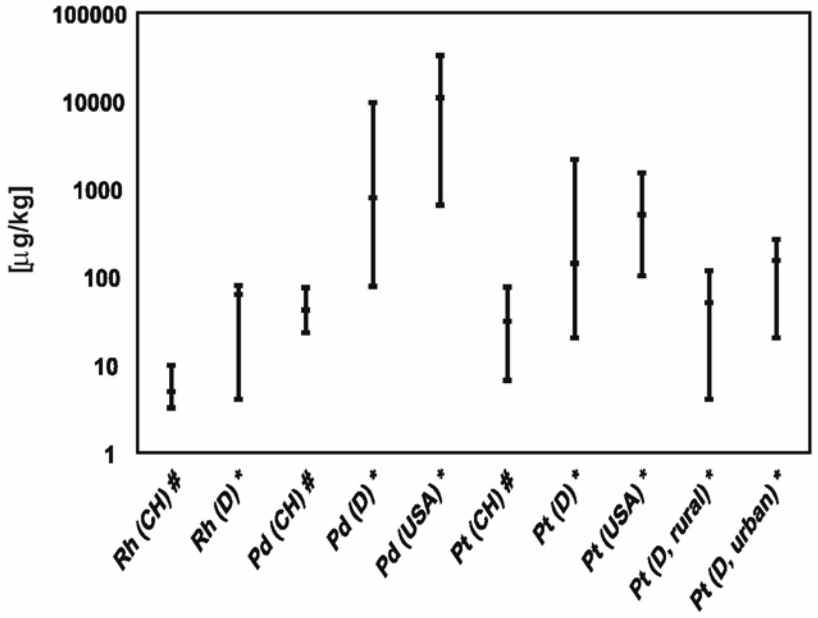


Fig. 3.3.2. Comparison of the average PGE content of different sewage sludge samples of different countries (#this study,* Lottermoser 1994)

(1994) reported data of sludges sampled in more than 30 German cities. Concentrations ranged from 38 to 1000 µg /kg d.m. for Pd and <10 to 130 µg /kg d.m. for Pt, respectively.

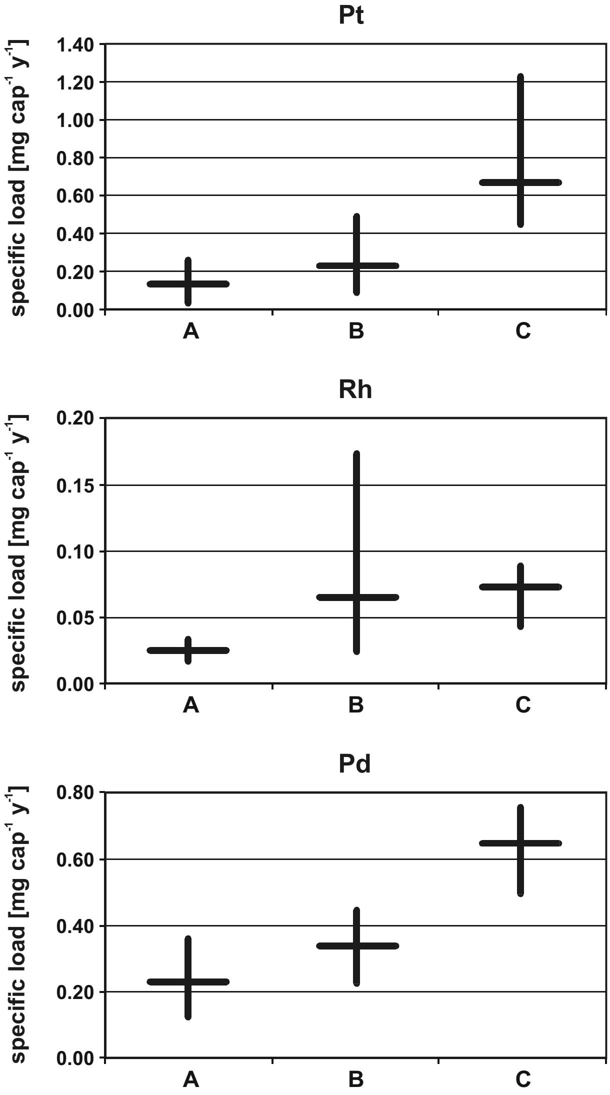


Fig. 3.3.3. Specific loads (mg/connected inhabitant per year) of PGE (maximum, mean, minimum) on different types of monitoring sites (A: n=5; B: n= 6; C: n=5)

Trace elements determined in sewage sludge are highly variable and thus the samples exhibit a range of element values (Table 3.3.2). Maximum concentrations are given e.g. for Zr (1148 mg/kg for C7), Br (315 mg/kg for A11), Pb (274 mg/kg for C4), Cu (971 mg/kg for A15), and Zn (2064 mg/kg for A16). The range of element concentrations of the investigated sludges is broadly similar to those of municipal sewage sludges documented by other authors (e.g. Lottermoser 1992). The high concentrations are very likely caused by applications of these elements in industry or craft industry and their subsequent discharge into the municipal sewer systems.

Mean specific loads calculated for Pd, Pt and Rh were at 344, 282 and 46 $\mu g\ cap^{-1}\ y^{-1}$, respectively (Fig. 3.3.3). A clear increase from site A to C can be observed. Loads of site A are most likely the result of background exposure of humans, e.g. due to release from dental alloys (Begerow and Dunemann, 2000). As the emissions of silver from dental alloys are causing dental medical problems, Au-Pd-alloys free of silver were developed and introduced into the market since 1982 (Knosp, 1995). The number of dental "Pd-based-alloys" commercialized on the German market increased from 10 in 1981 to 115 in 1993 (German Dental Vademekum). Therefore, it can be expected that private households increasingly release Pd mainly caused by dental applications and thus, Pd loads in sewage sludge are on the rise (Helmers et al., 1998). Additionally, Laschka (1996) has investigated noble metals in municipal sewage sludges from Munich. She found a positive correlation between Pt and Au in the primary sludges, which was attributed to the application of both of these metals in dental laboratories and surgeries.

Higher loads of sites B and C are induced by surface runoff which contains PGE emissions originating from catalysts. Higher loads on site C compared to sites of type B might be due to applications in industry or higher traffic emissions on these more urban sites. The origin of PGE in sewage sludge was further evaluated by other methods.

Cluster analyses using ward method (R-mode hierarchical cluster analysis) determined 7 different clusters reflecting different sources of elements (Fig. 3.3.4):

i. geogen source including Sn, Zr, Rb and As,
ii. partly caused by automobile emission grouping Zn, Cu, Pb, Sb,
iii. inorganic precipitates such as Mn, Ni, Fe and Ti,
iv. processes within the sewage sludge (Br, Cd, Zn) influenced by organic reactions
v. street runoff including Pt, Pd, Rh, Ba, Sr, Ca
vi. PGE forming a single cluster and
vii. elements such as Sr, Ba and Ca characterizing the street construction material

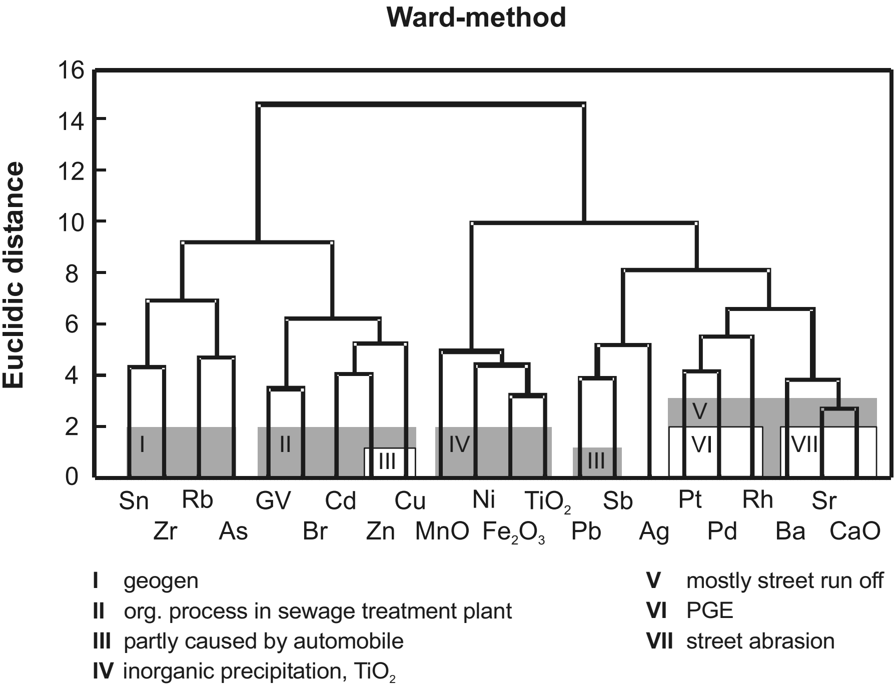


Fig. 3.3.4. R-mode hierarchical cluster analyses using the euclidic distances as similarity measure and Wards agglomeration methods of the chemical composition of sewage sludge samples and resulting groups of elements

Sewage sludge characterizes a mixture of different emission sources. A study of the Pt content of sludge ash produced by the combustion plant of Stuttgart showed Pt contents at approx. 80 µg/kg till 1987 and increased to about 100 µg/kg, resulting in an annual increase of the Pt load of 1.3 kg Pt per year until 1994 (Helmers et al., 1994). This indicates a strong increasing effect of the automobile catalyst. Plotting Sb versus Pt/Rh highest values correlate with the typical Pt/Rh ratio of around 6 (Fig. 3.3.5) which is due to traffic emission. Using Q-mode statistics on the base of the trace elements, Cu, Zn, Sb, Sn, Pb, Pt, Pd and Rh and the ratios of Pt/Rh and Pd/Pt samples of the sites of type A cluster a group distinct from type B and C reflecting different mixtures of source contamination (Fig. 3.3.6).

The study carried out by Lottermoser (1994) has shown that besides PGE release induced by traffic, urban sludges contain Pd from individual local industries. Fig. 3.3.7 summarizes the different emission sources and reasons for noble metals increase and trace element accumulation due to the

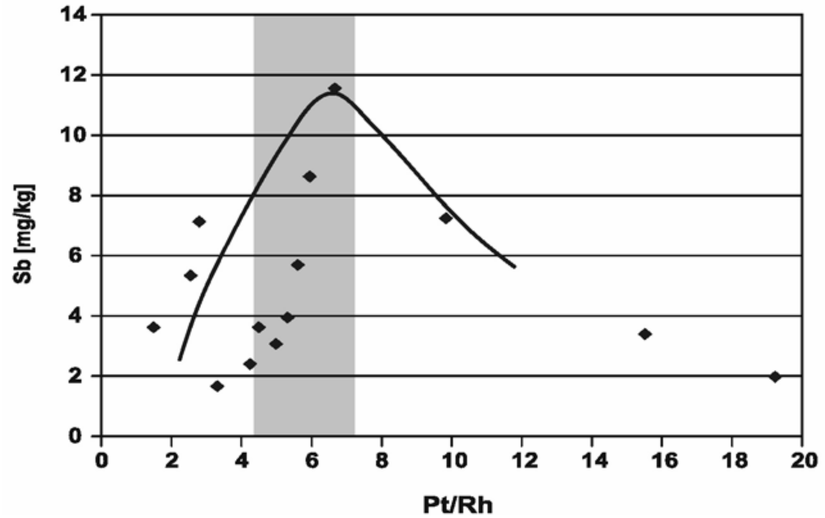


Fig. 3.3.5. Sb content versus Pt/Rh ratio (dash field reflecting typical traffic related Pt/Rh of around 6)

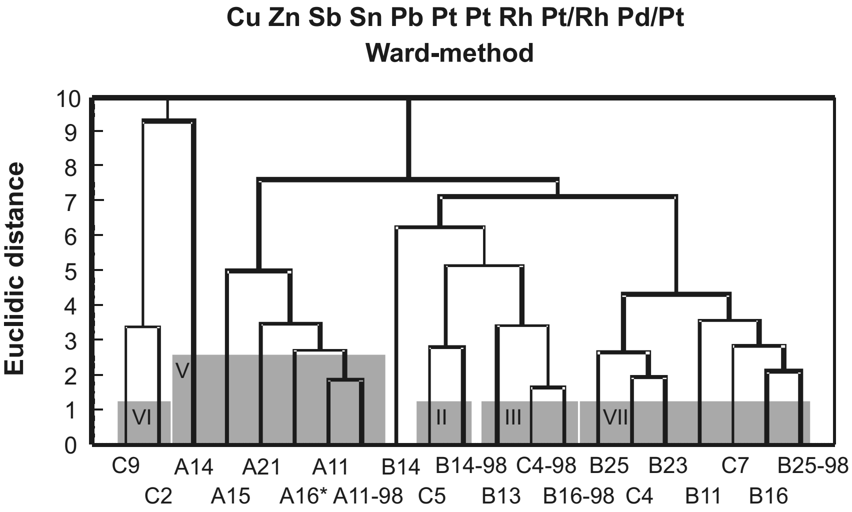
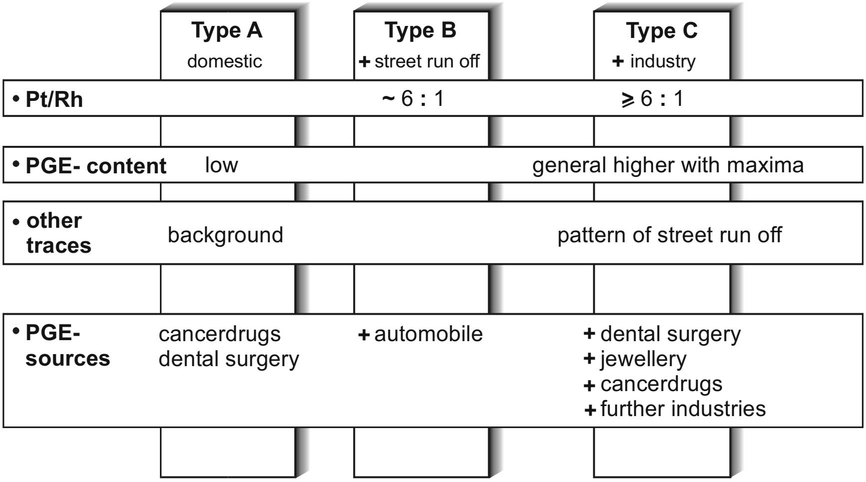


Fig. 3.3.6. Q-mode hierarchical cluster analysis using the euclidic distances as similarity measure and Wards agglomeration method based on traffic related elements

different types of collector systems and activities in the catchment area. Type A representing sewage sludge which contains particularly compounds



	Type A domestic	**Type B** + street run off	**Type C** + industry
• **Pt/Rh**		~ 6 : 1	⩾ 6 : 1
• **PGE- content**	low		general higher with maxima
• **other traces**	background		pattern of street run off
• **PGE- sources**	cancerdrugs dental surgery	+ automobile	+ dental surgery + jewellery + cancerdrugs + further industries

Fig. 3.3.7. Interpretation of sewage sludge samples based on chemical composition

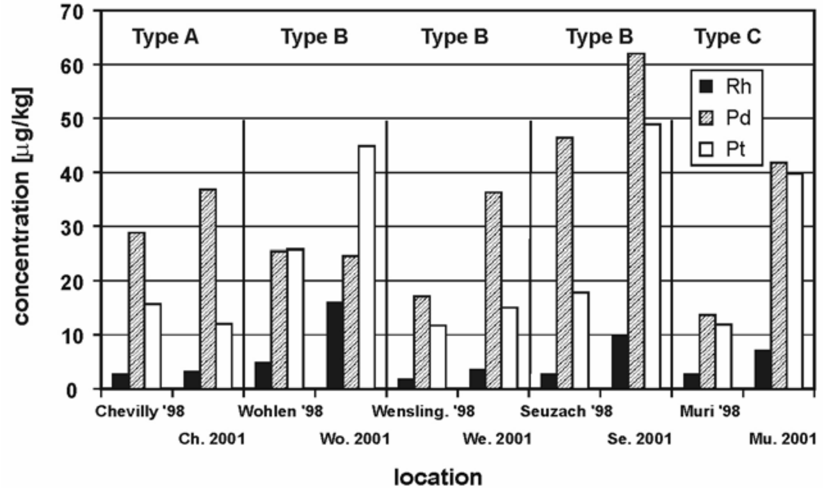


Fig. 3.3.8 Column diagram of Pd, Pt and Rh content for the three types of samples taken in 1998 and 2001

released by private households has a low Pt/Rh ratio, an overall low PGE content and a trace metal content reflecting background values. On these sites, the sources of the PGE are dental surgery and cancer drugs. Type B showing a mixture of domestic sewage and street runoff is characterized by a typical Pt/Rh ratio of around 6, the PGE content is generally enriched compared to type A samples and the trace element pattern reflects typical street runoff contamination. The PGE pattern of type B is overloaded by automobile emissions. Type C receiving sewage of a mixture of domestic, street runoff and industrial emission is characterized by higher Pt/Rh ratios of >6 and generally higher PGE contents.

The last step of the monitoring study consisted of the characterization of the time-depending trend of Pd, Pt and Rh (Fig. 3.3.8). At almost each location independent of the type of site, a clear increase from 1998 to 2001 can be observed for all noble metals especially for Pd at sites of type C which accounts for approximately 200%. Comparing Pt/Rh and Pd/Pt ratios from 1998 to 2001 (Fig. 3.3.9) variable trends occur which reflect the different increase of emission sources and the higher influence of the use of Pd in daily life and the higher contamination. Type A shows a decrease in Pt/Rh but an increase in Pd/Pt. Type C exhibits an opposite trend for Pt/Rh. Type B behaves like type A for Pt/Rh but shows no general trend for Pd/Pt. This typically characterizes the overall trend in the consumption of Pd and Pt.

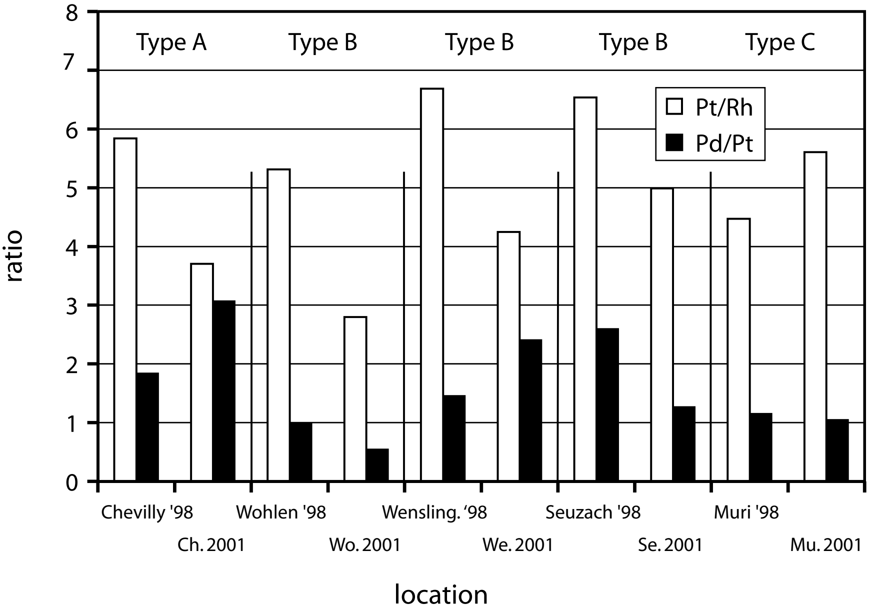


Fig. 3.3.9. Column diagram of Pt/Rh and Pd/Pt for the three types of samples taken in 1998 and 2001

3.3.6 Conclusions

Within the present study it has been shown that sewage sludge is an appropriate matrix to track environmental relevant compounds such as PGE if the characteristics of the catchment area and the technology of the WWTP are accurately defined. Different methods have been used for the identification of their sources: specific loads, cluster analyses using ward method and PGE patterns from different types of monitoring sites. The results were consistent regarding the origin of PGE. Specific loads of Pd from private households observed on sites of type A are likely to be due to dental alloys. Higher loads of PGE on sites of type B are mostly related to traffic emissions. This was confirmed by cluster analysis, correlation between Sb and a Pt/Rh ratio of around 6 as well as PGE patterns. A mixture of domestic, street runoff and industrial emissions occurring on sites of type C resulted in Pt/Rh ratios of >6. Between 1998 and 2001, an increase of Pd in sewage sludge was observed indicating that emissions are on the rise mainly due to changes in PGE composition of autocatalysts.

Acknowledgements

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3.4 The Importance of Assessing Variability in the Distribution of Anthropogenic Palladium, Platinum and Rhodium in Fluvial Sediments

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Abstract

The distribution and behaviour of anthropogenic platinum-group elements (PGE) in river systems has as yet attracted little attention. Aquiring good quality data in PGE analysis poses a serious challenge to the environmental chemist, not in the least due to the low concentrations at which the PGE are currently found in the environment. Using the River Stour in Kent, U.K. as a case study, the work presented in this paper focuses specifically on the spatial and temporal variability of PGE in fluvial sediments. The analysis of river bed sediments shows high variability both on a catchment scale and on a local scale within sample sites. Moreover, high relative standard deviation points to a heterogeneous distribution of PGE within sediment samples, which is characteristic of the elements and is commonly known as the nugget effect. If unassessed, analytical data are unlikely to be truly representative and the interpretation of PGE data could be inherently flawed. For this reason this paper suggests a need to include thorough quantification and reporting of this variability as a matter of practice in the acquisition of environmental PGE data.

3.4.1 Introduction

The specific application of platinum-group elements (PGE) as catalysts in vehicle emission control devices is causing significant redistribution of these precious and potentially harmful elements to the wider environment (Artelt *et al*, 1998; Farago *et al*, 1995; Higney *et al*, 2002). The distribution of palladium, platinum and rhodium has been studied intensively in roadside environments for the last 20 years, resulting in an extensive body of data on levels of PGE in various environmental matrices. However, despite the growing knowledge of PGE concentrations in the environment, it remains difficult to assess their quantitative impact and make accurate predictions of their behaviour after emission.

The role of rivers in the redistribution of anthropogenic PGE has as yet received little attention. Rivers have a predominant role in the transfer of various natural and anthropogenic particulates and compounds from the continents to the sea. River sediments in particular incorporate pollutants from a wide range of sources and can simultaneously act as sources, sinks and transport pathways. Evidence of an increased flux of palladium and platinum to estuarine and coastal environments is abundant (Edwards and Quinn, 1998), yet the behaviour of these elements in estuaries and in the river systems that serve as suppliers to these environments is largely unknown. The challenge to the environmental chemist now lies in understanding the chemical and physical transport processes involved in the transfer of this material to the coastal environment. When PGE are determined, their source is sometimes deemed easy to establish; for example roadside environments habitually reflect the Pt/Rh signature in which these metals are applied to automobile catalyst (Pt/Rh ~ 5:1). Tools such as PGE ratios are very useful in the interpretation and modelling of PGE data. However, due to the inherent uncertainty of determining a metal concentration, the ratio calculated from these concentrations has an uncertainty also. McDonald (1998) pointed out that this uncertainty is generally ignored and yet changes in ratios are increasingly used to explain geochemical behaviour of PGE or to differentiate between possible PGE sources (McDonald *et al*, 1995; Pattou *et al*, 1996).

Metals in river bed sediments are inevitably subject to a wide range of physical, chemical and biological processes, which cause variations in the concentrations in terms of time and space**.** In order to model the physical and chemical processes controlling PGE behaviour, it is essential that the chemist has access to reliable data, which take into account any sources of error and variability. Supported by a case study in the River Stour, Kent, U.K., the principal aim of this paper is to assess the extent of analytical variability in PGE analysis of sedimentary materials and to evaluate spatial and temporal variation in the distribution of PGE in river sediments. The present study follows on from the previous work of de Vos *et al,* (2002), which identified a number of natural and anthropogenic sources of PGE in the Stour catchment. This previous study enabled selection of the sites investigated in detail here.

3.4.2 Methodology

The methodology for sample collection of the sediments of the River Stour in 1999 was outlined in de Vos *et al.* (2002). Sampling for the new survey reported here was carried out in June 2001. Samples of river bed sediment were taken using a Birge-Eckman grab sampler at sites along the Great Stour tributary and the main river channel from Ashford to Sandwich (numbered arrows in Fig. 3.4.1). In the original baseline survey carried out in 1999, 22 sample sites were selected on the basis of land use variation. For the present work the number of sites was reduced to 8; the exact locations of the selected sites are identical to those of the 1999 survey. At these sites, a minimum of two replicate samples were collected, at a maximum of 5 meters distance from each other. All samples were prepared by NiS fire assay with Te coprecipitation and ICP-MS. For details on the analytical methodology and data quality assurance the reader is referred to Koeberl *et al.* (2000) and Huber *et al.* (2001).

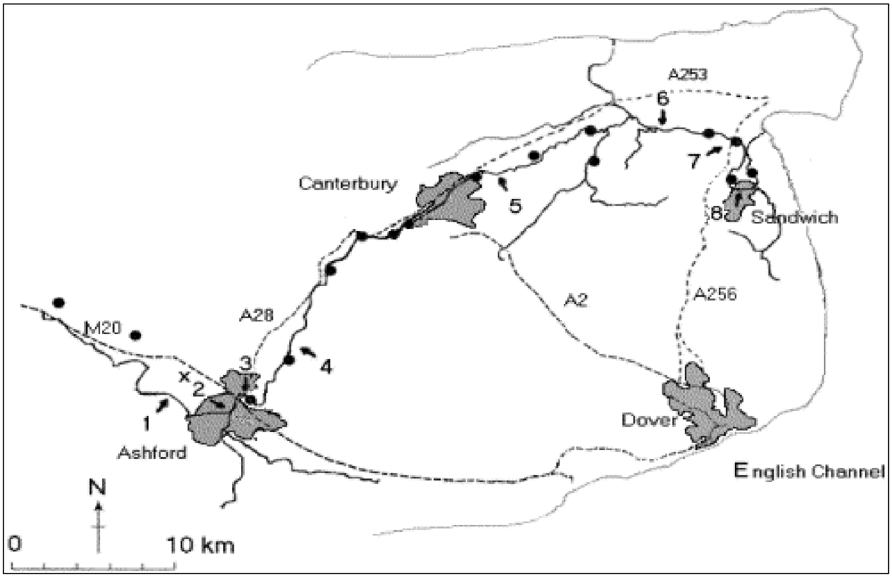

Fig. 3.4.1. Map of the River Stour catchment, showing watercourse (solid black line), numbered sample location (arrows), urban areas (grey shading), roads (dotted lines), M20 Catchpit (X) and urban and rural sewage outlets (circles)

3.4.3 Results and discussion

Internal variability of PGE distribution

The PGE data from the new survey and those relevant from the 1999 survey are presented in Table 3.4.1. Sample locations are labelled by the number corresponding to the sites marked by arrows on Fig. 3.4.1. All samples collected in 1999 are marked by an asterisk. Samples collected in 2001 are marked by numbers 1 to 3, indicating the sample replicates taken within sample locations.

Platinum and Pd are present in most samples and at the highest concentrations, whereas Rh concentrations are generally much lower and often below the limit of detection. The results show there is a high variability among sample replicates. The relative standard deviation (defined as (standard deviation/mean) *100%) varies from 3% to over 100% (marked as non-quantifiable (n.q.) in Table 3.4.1). Other studies looking at the concentration of PGE in stream sediments show similarly high coefficients of variation (from 75% for Pd to 100 % for Ir, Holdham *et al.* 1994), and indicate abrupt changes in concentration within a short distance (Dissanayake *et al*, 1984), suggesting that high variability is inherent to the nature of the elements. An issue particular to the distribution of the PGE is that they are less evenly distributed within rocks and related materials compared to other trace elements. They are often present as sub-micron-sized platinum-group minerals (PGM), or they collect as trace components in very specific solid sulphide or oxide phases (Barnes *et al.* 1985). This characteristic heterogeneous distribution where the distribution of an element in a sample is controlled by a small number of particles has been termed the 'nugget effect'(e.g. Potts, 1987). During weathering of these PGM, their behaviour is predominantly controlled by mechanical processes. Although some chemical leaching may take place, the PGM will be released, transported and deposited primarily in particulate form (*e.g.* Mardock and Barker, 1991), thus maintaining their heterogeneous distribution in sedimentary environments.

The nugget effect may be an acceptable explanation for the high variability in PGE distribution in natural weathering systems. In contrast, the PGE in the sediments of the Stour are found to be of mainly anthropogenic origin. The question is if the nugget effect can account for the high standard deviations found in the River Stour sediments. The answer to this question must be found in the way the metals enter the river system. However, the chemical form in which anthropogenic PGE are emitted from various sources and transported is poorly understood.

Table 3.4.1. PGE concentrations of the bed sediments of the River Stour, Kent collected in 1999 (marked *) and in 2001 (in ng/g)

	Pt	Pd	Rh	PGE Total	Pt/Pd	Pt/Rh
1. Worten *	0.45 ±0.17	0.30±0.05	<0.11	0.75	1.5±0.6	-
Worten 1	1.23±0.07	0.45±0.31	<0.11	1.68	2.73±1.9	-
Worten 2	n.q	n.q.	<0.11	-	-	-
2. GSA *	4.23±0.11	5.50±1.81	0.23±0.02	9.96	0.8±0.3	18.4±1.7
GSA 1	7.87±2.89	0.72±0.46	1.31±0.31	9.9	10.93±8.1	6.00±2.6
GSA 2	8.40±0.42	n.q.	<0.11	8.52	70.00±99.2	-
GSA 3	3.55±1.65	0.32±0.15	<0.11	3.87	11.09±7.3	-
3. Ashford *	0.74±0.31	0.25±0.12	<0.11	0.99	3.0±1.9	-
Ashford 1	63.55±13.05	9.01±0.41	4.41±1.27	76.97	7.05±1.5	14.41±5.1
Ashford 2	41.62±9.18	4.88±0.52	4.25±3.61	50.75	8.53±2.1	9.79±8.6
4. Wye *	3.33±2.85	n.q.	<0.11	3.33	-	-
Wye1	<0.29	<0.16	<0.11		-	-
Wye2	10.71±3.15	<0.16	2.03±0.66	12.74	-	5.27±2.3
Wye3	<0.29	<0.16	<0.11		-	-
5. Fordw *	4.42±4.33	n.q.	n.q.	4.42	-	-
Fordw. 1	0.78±0.13	<0.16	<0.11	0.78	-	-
Fordw. 2	0.59±0.1	<0.16	<0.11	0.59	-	-
6.Stodm.*	3.46±0.58	2.23±0.04	0.26±0.01	6.7	1.6±0.3	13.3±2.3
Stodm. 1	3.02±0.81	9.36±2.86	<0.11	12.38	0.32±0.1	-
Stodm. 2	2.35±0.99	7.02±1.11	<0.11	9.37	0.33±0.1	-
7.Haff. *	1.55±0.89	5.71±4.32	<0.11	7.26	0.3±0.3	-

(Part 1 of 2)

The most important sources of PGE identified in the Stour catchment are atmospheric deposition of traffic-related PGE and direct inputs of sewage discharge during storm events (de Vos *et al.* 2002). The first report concerning direct measurements of traffic-emitted PGE species is the work of

Table 3.4.1. PGE concentrations of the bed sediments of the River Stour, Kent collected in 1999 (marked *) and in 2001 (in ng/g)

	Pt	Pd	Rh	PGE Total	Pt/Pd	Pt/Rh
Haff. 1	0.91±0.15	2.15±0.43	<0.11	3.06	0.42±0.1	-
Haff. 2	1.56±0.31	1.99±0.33	<0.11	3.55	0.80±0.2	-
Haff. 3	1.95±0.33	2.79±0.21	<0.11	4.74	0.70±0.1	-
8. Sandw. *	1.13±0.16	0.93±0.14	<0.11	2.06	1.2±0.2	-
Sandw. 1	8.96±0.79	2.25±0.1	1.56±0.37	12.77	3.98±0.4	5.74±1.5
Sandw. 2	n.q.	3.37±2.06	0.59±0.56	3.96	-	-

(Part 2 of 2)

n.q.: not quantified because uncertainty higher than concentration found;
GSA= Great Stour Ashford; Stodm.= Stodmarsh; Haff.= Haffendens; Fordw= Fordwich;
Sandw.= Sandwich
* Samples collected in 1999, data from de Vos *et al*, 2002
1,2,3: represent sample replicates of sediments collected in 2001

Schlogl *et al.* (1987), who were able to detect Pt in particles from exhaust gas by surface analysis. The particles were mainly present as the original Pt(0) form, accompanied by small amounts of Pt^{4+} in possible oxidic species, which was interpreted as an alteration. A number of publications support this claim, showing that although the amount of soluble Pt in exhaust fumes of fresh gasoline and diesel catalysts can be significant, the main release of Pt into the environment from fresh gasoline catalysts is as particulates (Konig *et al*, 1992; Wei and Morrison, 1994; Moldovan *et al*, 2002). Palladium and Rh are released in broadly equivalent amounts of soluble and particulate species (Moldovan *et al*, 2002).

The chemical speciation of the PGE in sewage sludge remains poorly constrained and is controlled by the original form in which it was emitted by the primary waste source. Sources of PGE in sewage sludge include industrial (e.g. photographic laboratories, production of fertiliser) and domestic (e.g. abrasion of jewellery) sources, medical applications (dentistry, hospitals) and road runoff. As a result, PGE can be expected to be present as a mixture of particulates, as adsorbed elements on suspended particulate matter, as colloids and as dissolved organic and inorganic complexes (Lottermoser and Morteani, 1993). Natural waters are capable of transporting only very little PGE as soluble species (Westland, 1981), so precipitation caused by microbial activity, reactions with organic matter, decreases in ligand concentration and adsorption onto sulphides and organic material are likely to result in the rapid and efficient concentration of platinoids onto organic sewage particles in municipal wastewater systems (Lottermoser and Morteani, 1993).

The nature of the sources descibed above strongly suggests that the majority of the PGE emitted into the Stour will be transported as, or associated with, particulates. Consequently, the PGE concentration determined from any single aliquot is strongly influenced by statistical variations in the number of PGE-rich particles a sample contains (Van Loon, 1984). The heterogeneous distribution that this produces, implies that if the PGE are primarily present as particulate species, the nugget effect will be a significant source of internal variability in analytical data and this will significantly affect the determination of anthropogenic PGE concentrations and ratios in environmental samples. The extent to which this effect can be minimised and representative PGE concentrations obtained from any individual sample aliquot is dependent on: (1) the initial distribution of individual PGE between the different PGE-rich phases and the size fractions in which the PGE are concentrated, (2) the average particle size in the crushed sample and (3) the mass of sample analysed (larger test portions should contain greater numbers of PGE-rich particles and thus average out statistical variations). Different sample preparation and analysis methods will vary factors (2) and (3), but are unlikely to completely eliminate factor (1).

The discovery and study of the anthropogenic redistribution of PGE has resulted in the development of an abundance of sample preparation methods (Bencs *et al*, 2003). Unfortunately, the heterogeneity of PGE distribution is often disregarded in the design of these methods. Many analytical procedures use less than 1 gram of sample (Colodner *et al*, 1992; Wei and Morrison, 1994; Holdham *et al*, 1994); the sample size used for this work is 15 grams, yet the distribution of PGE in some of the Stour sediments is so great that even this sample size can not sufficiently compensate for the nugget effect. Potts (1987) and Plessen and Erzinger (1997) have concluded that it may be impossible to entirely homogenise the PGE in geological materials even using the mass of test portion commonly used in fire assay analysis (up to 50 grams). Therefore, regardless of how precise the actual analytical procedure is, there will always be a residual uncertainty over how representative any selected powder aliquot is representative to the whole sample. This uncertainty can only be quantified by replicate analyses (McDonald, 1998).

Spatial and temporal variations in PGE distribution

The data in Table 3.4.1 show that the PGE concentrations in the sediments of the River Stour exhibit significant spatial and temporal variations. The spatial variation is found not only on a catchment scale between sampling locations, but also on a local scale within a cross-section of a sampling site. Wye is an extreme example: sample 'Wye 2' shows one of the highest Pt concentrations found in the entire river, yet the other samples collected at this site show concentrations below the limit of quantification (LOQ). Spatial variability in a cross-section is largely dependent on parameters such as sediment particle size, turbulent flow conditions, seasonality of flow and channel morphology (Droppo and Jaskot, 1995). The data suggest that the majority of samples in the upstream regions of the Stour show similar heterogeneous distribution within sites, while this trend is not so pronounced in the downstream section of the river. The PGE may be present here as finer particulates that are more evenly distributed in the sediment. Alternatively, the dynamic nature of the estuary may homogenise the distribution of PGE throughout this section of the river. At this point such a statement must be treated with some degree of caution because of the limited number of sites sampled. Nevertheless, the spatial variability of PGE distribution at a particular location in the river is potentially very high. Moreover, the extent of variability is not necessarily uniform throughout the length of the river. Therefore, collecting one sample at a location can not be taken as representative of the PGE concentration at that location.

The temporal variability of PGE concentrations in river sediments has an equally significant influence on the interpretation of PGE data. Comparing the data from 1999 and the data from this survey, significant changes have occurred in the PGE concentrations found at particular locations. At a number of sites the total PGE concentration has decreased (Worten Mill, Great Stour Ashford (GSA), Haffendens), whereas other locations have seen a dramatic increase in total PGE concentrations (Ashford sewage treatment works (STW), Wye, Sandwich). The increase at Ashford STW is the most remarkable. Due to the proximity of the STW, this location will receive excessive sewage discharge during storm events. Moreover, this is the confluence of the Stour with a tributary that receives the drainage waters of a sediment retention lagoon along the M20 (see Fig. 3.4.1). The months preceding the 2001 sample collection saw higher rainfall and increased flow conditions in the main river channel compared to 1999 (www.nwl.ac.uk). High energies and flow rates associated with storm events are known to remobilise high quantities of sediments and associated pollutant from catchpits and urban gullypots (Morrison *et al*, 1989). In this manner, storm discharge from the STW and the lagoon has resulted in the extreme accumulation of PGE at this location. In contrast, , the PGE concentrations found at this location in 1999 were significantly lower, with no detectable Rh, giving the impression that the river was little affected by the lagoon and the STW at that time.

The example above is a stark illustration that sampling at different times can produce significantly different PGE data, as PGE sources become involved or isolated at different times. A single sampling event can only provide a snapshot of the system at a given time, and does not allow an interpretation of how the system can change. The extent of variability seen in the data in Table 3.4.1 highlights the error that single sample collection events can introduce on the interpretation of PGE data.

3.4.4 Conclusions

The work presented in this paper illustrates clearly the extreme variability in PGE distribution in fluvial sediments. The characteristic ‘nugget effect’ of the PGE forms an additional problem to the high potential for spatial and temporal variability inherent to the distribution of trace elements and other components in fluvial sediments. As a consequence, single point sampling programmes can be prone to serious interpretative error and utterly misrepresent the true distribution of PGE. Further processing of such data in a model will lead to erroneous conclusions. Moreover, the problems of data heterogeneity as demonstrated here suggests that comparison of PGE data from two or more separate studies must be undertaken with extreme caution and may , in fact, be meaningless.

In order to model the physical and chemical processes controlling PGE behaviour, it is essential that all sources of error and variability are taken into account. Therefore, sampling and analytical programs have to be designed in such a way that allows the spatial and temporal changes in PGE distribution to be quantified and reported. The quantification of this variability then ensures more confidence in the interpretation and modelling of the PGE behaviour in environmental systems.

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3.5 Man-Induced Changes of Palladium in Polar and Alpine Snow and Ice Archives

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3.5.1 Introduction

Dated snow and ice that has accumulated in polar ice caps and high altitude temperate glaciers have proven to be very valuable archives of past natural and man-induced changes in the occurrence of heavy metals in the atmosphere of our planet. This was beautifully illustrated, for instance, by studies of lead and copper in Greenland ice dated from the time of the Roman Empire, which evidenced an early large scale pollution of the atmosphere of the Northern Hemisphere for these two metals two millennia ago, at the apogee of the Roman civilization (Hong et al. 1994; Hong et al. 1996). Another example is the evidence of a widespread pollution of the most remote areas of the Southern Hemisphere by various heavy metals, which was obtained through the analysis of snow deposited in Antarctica since the middle of the 19th Century (Planchon et al. 2002; Planchon et al. 2003). A last example is the recent study of various heavy metals in snow and ice cores drilled at Colle Gnifetti, a high altitude glacier saddle in the Italian-Swiss Alps, close to the summit of Monte Rosa. It allowed us to obtain the first reconstruction of past changes of European emissions of heavy metals to the atmosphere from the 1650s (Barbante et al. 2004; Schwikowski et al. 2004). Finally, it should also be mentioned that the analysis of very ancient ice dated from previous climatic cycles can provide us with extremely interesting data on past natural concentration of heavy metals in the atmosphere and their variations as a function of climate (Gabrielli et al. 2004; Hong et al. 2004; Vallelonga et al. 2005).

It is very interesting to determine palladium in these very valuable archives, as anthropogenic emissions of palladium to the environment have increased dramatically until late 1990s, especially because of the use of this metal in automobile catalytic converters (Barbante et al. 2001; Hoppstock and Sures 2004; Johnson Matthey, various issues, 1987-2004). Studying changes of palladium in snow and ice from Greenland, Antarctica and mid latitude ice fields dated from the post industrial revolution period, will allow an improved assessment of the importance of the pollution of the atmosphere by this metal, on both a global and regional scale. Moreover, the evaluation of palladium concentrations in very ancient ice dated from before any human influence will allow an improved understanding of the contribution from various natural sources and provide us with natural reference levels against which modern trends can be assessed.

3.5.2 Field sampling and dating of snow and ice samples

Shallow snow down to a depth of ~ 10 m can be collected in the field, either from the walls of snow pits or as snow cores (Boutron 1995). Great precautions must however be taken to prevent contamination of the samples since palladium concentrations in polar or Alpine snow are extremely low (just to give an example, the palladium concentration in Greenland snow dated from the 1970s is ~ 0.2 pg g^{-1}, where 1 pg stands for 10^{-12} g (Barbante et al. 2001)). For instance, sampling pits must be dug by operators wearing clean room clothing, using special tools that have been extensively cleaned with acids in clean rooms (Planchon et al. 2001). The samples are extracted from the walls of the pits using acid-cleaned containers made of plastics, such as low density polyethylene (LDPE). The snow cores are drilled using special hand-operated augers made of plastics such as polycarbonate, which have been extensively cleaned with acids in clean rooms (Boutron et al. 1991). The time periods, which can be covered by such shallow samples is however limited: just to give an idea, the snow at a depth of 10 m was deposited about 30 years ago at Summit in Central Greenland and about 200 years ago at Dome C in East Antarctica.

If older snow and ice are to be obtained, the only way is to use electromechanical or thermal drills (Boutron 1995). They provide us with snow or ice cores that are always contaminated on the outside during drilling operations. This contamination is especially important for deep ice that can only be obtained from drilling holes that are filled with wall-retaining fluids (a mixture of kerosene and CFC or CFC substitutes). Such cores need to be decontaminated by chiselling veneer layers in progression from the outer contaminated layers to the center, in order to obtain the uncontaminated inner part of the core (Candelone et al. 1994; Barbante et al. 1999).

Dating of these snow and ice samples can be obtained using various methods which fall into four main categories: i) layer counting; ii) use of time markers and correlation with other dated time series; iii) comparison with insolation changes; iv) glaciological modeling. These different methods are described in some detail in various papers, for instance (Hammer 1989; Reeh 1989; Stauffer 1989; Boutron 1995; Southon 2002; Parrenin et al. 2004).

3.5.3 Determination of palladium in polar and Alpine snow and ice

If fully reliable data are to be obtained, analyses must be performed inside special clean laboratories (Boutron 1990; Planchon et al. 2001; Vallelonga et al. 2002). Of particular importance is the ability to produce ultrapure water and acids, which are used specifically for cleaning of the material that will be used throughout the analytical procedure and for the preparation of ultra-low concentration standard solutions. To give an example, palladium concentrations in the ultrapure water produced by ion-exchange resins in our clean laboratories, are ~ 0.3 pg g^{-1} (Barbante et al. 1999).

Our preferred method for the determination of palladium in polar and Alpine snow and ice is Inductively Coupled Plasma Sector Field Mass Spectrometry (ICP-SFMS). Various samples have been successfully analysed for palladium down to the sub pg g^{-1} concentration range using Element or Element2 instruments from the Thermo Electron Corporation (Bremen, Germany) using a micro-flow (< 100 µl min^{-1}) nebulisation system that allowed us to analyse only a few ml of the samples, just after melting at room temperature and acidification to 1% (*v:v*) with ultrapure nitric acid (Barbante et al. 1999; Gabrielli et al. 2004). A recent improvement lies in the coupling of the Element2 instrument with a micro-flow nebulisation/ desolvation sample introduction system (Aridus, Cetac Technologies, Omaha, NE, USA) (Field and Sherrell 2003; Gabrielli et al. 2004). It significantly reduces solvent based spectral interferences linked with the formation of oxides in the plasma, resulting in an improved signal to background ratio.

Special consideration was given to all the potential interferences that could hamper the accurate determination of palladium, which was based on the measurement of the ^{105}Pd and ^{106}Pd isotopes, as discussed in details in (Barbante et al. 1999). The most critical possible interfering species for ^{105}Pd are: ^{40}Ar^{65}Cu, ^{36}Ar^{69}Ga, ^{89}Y^{16}O, ^{88}Sr^{17}O, ^{87}Sr^{18}O, ^{87}Rb^{18}O, ^{52}Cr^{53}Cr; for ^{106}Pd possible interfering species are: ^{40}Ar^{66}Zn, ^{38}Ar^{68}Zn, ^{36}Ar^{70}Ge, ^{90}Zr16O, ^{88}Sr^{18}O, ^{89}Y^{17}O, ^{106}Cd, ^{87}Rb^{18}OH and ^{40}Ar^{65}CuH.

Typical detection limits for palladium were found to be ~ 0.08 pg g^{-1} (Barbante et al. 1999). This means that the direct determination of palladium in most samples is possible, except for ancient ice dated from interglacial periods, for which a pre-concentration step (by sub-boiling evaporation (Gabrielli et al. 2004)) was necessary. An estimation of the instrumental repeatability of the data obtained from consecutive measurements of Alpine snow samples gave a relative standard deviation of ~ 30 % for both isotopes.

3.5.4 Palladium in Greenland snow dated from the last decades and ancient Holocene ice

The very first time series of palladium in polar snow and ice was recently obtained by Barbante and co-workers (Barbante et al. 2001). They determined palladium in various snow and ice samples that were collected in Central Greenland at Summit (72°34'N, 37°37'W, elevation 3238 m, mean snow accumulation rate of 21.5 g water cm^{-2} yr^{-1}) as part of the European Eurocore, GRIP and TAGGSI programs. They especially included various snow samples covering the period 1969-1995, which were obtained from a 10.7 m snow core (Boutron et al. 1991) and a 2.7 m deep snow pit (Barbante et al. 2003). Also studied were two sections of the 3028.8 m GRIP deep ice core (Dansgaard et al. 1993) dated at 7260 and 7760 years ago (depths of 1230.4 and 1286.5 m, respectively). The two samples of ancient ice allowed an assessment of past natural-Holocene palladium concentrations before any anthropogenic input. The 1969-1975 samples were used to assess anthropogenic changes before the use of automobile catalytic converters, while the 1975-1995 samples were used to try to identify the possible influence of emissions from automobile catalytic converters. The results are shown in Fig. 3.5.1.

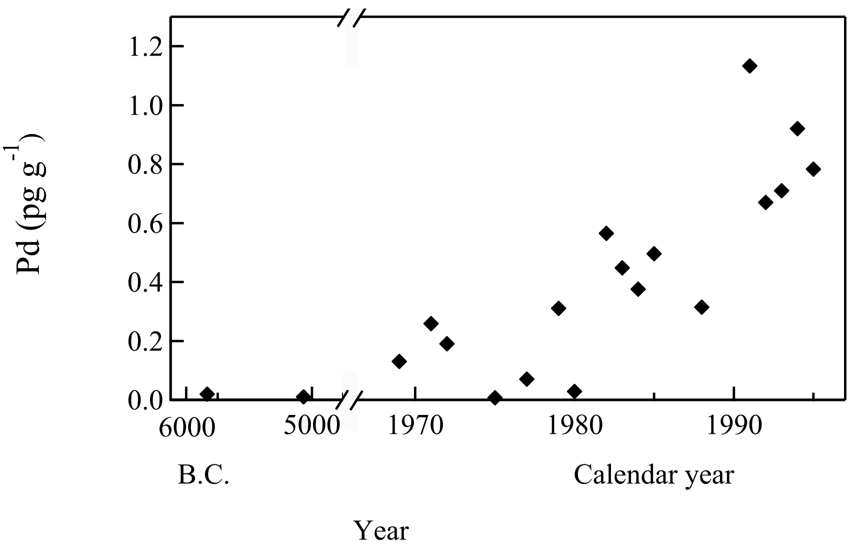

Figure 3.5.1. Changes in palladium concentrations in ice and snow from Summit, Central Greenland as a function of the age of ice and snow. From Barbante and co-workers (Barbante et al. 2001)

Seven millennia ago, palladium concentrations were extremely low in Greenland ice, about 0.01 pg g^{-1}. At that time, palladium only originated from natural sources, such as rock and soil dust (Wedepohl 1995), extraterrestrial dust (Gabrielli et al. 2004) and volcanoes (Zoller et al. 1983).

Fig. 3.5.1 shows that in the snow samples dated from 1969 to 1975, just before the introduction of automobile catalytic converters, palladium concentrations were about 0.1 ñ 0.2 pg g^{-1}, i.e. about one order of magnitude higher than natural levels. It shows that there was already a large-scale contamination of the atmosphere of the Northern Hemisphere for palladium in the early 1970s, which could be detected at a high altitude site (3238 m) in remote Central Greenland, far away from populated areas.

We are not aware of any published inventory of anthropogenic palladium emission to the atmosphere of the Northern Hemisphere for the early 1970s (and even for other time periods). An important source could be Platinum Group Metals (PGM) and nickel mining and smelting activities, especially in Russia and North America (Johnson Matthey various issues, 1987-2004). Emissions from Russian smelters, especially the huge nickel smelters in Norilsk, in the Russian Arctic, could be a very significant contribution to palladium in Central Greenland snow dated from the early 1970s since these emissions are probably quite important and a large percentage of air mass back trajectories reaching Summit, originate from the Russian Arctic (Kahl et al. 1997; Rauch 2005). Another source is likely to be the chemical industry, where palladium is used for palladium-based catalysts, for instance in the production of vinyl acetate monomer (VAM), purified terephthalic acid (PTA) and hydrogen peroxide, and for catchment gauzes in nitric acid production (Johnson Matthey various issues, 1987-2004). Other contributions could be from the incineration of refuse (for instance the incineration of waste containing electronic components such as multi-layer ceramic capacitors) or from the combustion of fossil fuels. No quantitative data are presently available for these different possible sources, but the Greenland data by Barbante and co-workers (Barbante et al. 2001) do show that they were intense enough to have strongly enhanced palladium concentrations above natural levels even in the most remote areas of the Northern Hemisphere.

Fig. 3.5.1 shows that during the twenty year period from 1975 to 1995, palladium concentrations continuously increased up to values of ~ 1 pg g^{-1}, i.e. values which are about 100 times above natural values found in ancient Holocene ice (Barbante et al. 2001). This increase appears to be rather steady with a rate of ~ 0.03 pg g^{-1} per year. Interestingly, these variations are quite different from those observed for platinum and rhodium, which have rather constant concentration values up to the late 1980s followed by a rather sudden increase between 1990 and 1995 (Barbante et al. 2001). Barbante and co-workers suggested that the steady increase observed for palladium, mainly reflects increasing emissions of this metal from mining and smelting, especially in the Russian Arctic. Conversely, they suggested that the contribution from emissions from automobile catalytic converters was still very limited during the time period covered by the samples (the most recent samples in this study were dated from 1995). As shown in Fig. 3.5.2, the palladium demand for automobile catalytic converters started to be significant only after about 1994, which means that a significant contribution from the emissions from automobile catalytic converters could only probably be detected in Greenland snow after the mid 1990s.

It is interesting to note that recent studies have investigated short-term (intra-annual) variations in palladium concentrations in Greenland snow (Barbante et al. 2003). The data were obtained by analyzing a comprehensive series of snow samples, collected from a 2.7 m deep snow pit near Summit in Central Greenland; they covered a continuous four year time period from spring 1991 to spring 1995. The chronology of the different seasons in the snow pit where deduced from the concentration profiles of sodium, calcium, sulphate and methane sulphonic acid. As illustrated in Fig. 3.5.3, pronounced intra-annual (seasonal) variations in palladium con-

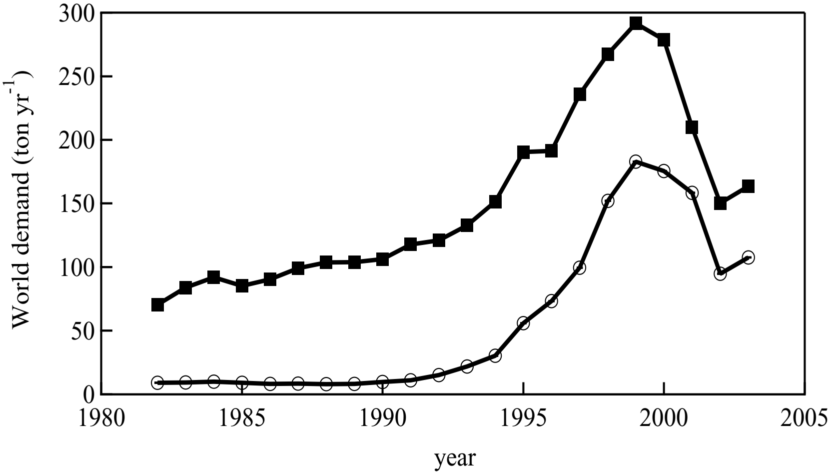

Fig. 3.5.2. Changes in palladium world demand since the early 1980s. Squares: total demand. Open circles: demand for automobile catalytic converters. From refs. (Barbante et al. 2001; Johnson Matthey various issues, 1987-2004)

centrations are observed in Greenland snow with elevated concentrations generally observed in snow deposited during spring. Possible explanations for these short-term variations are include changes in source areas and atmospheric transport patterns (Barbante et al. 2003).

3.5.5 Changes in palladium concentrations in high altitude Alpine snow and ice since the middle of the seventeenth century

Snow and ice cores drilled at high altitude locations in the Alps have the potential to provide us with very interesting information on past emissions of metals such as palladium during the most recent centuries in Europe. To obtain this valuable data, it is important that the drilling sites are carefully selected. It is especially mandatory that the site is at a high enough altitude (generally above about 4000 m) to have no significant melting of the snow layers during even the warmest months in summer since such melting would damage the record of changes in metal concentrations. Also, the glaciological conditions at the drilling site should allow for long enough time series to be obtained. Systematic investigations of possible drilling sites in the Alps have identified very few suitable sites. One of these sites is the

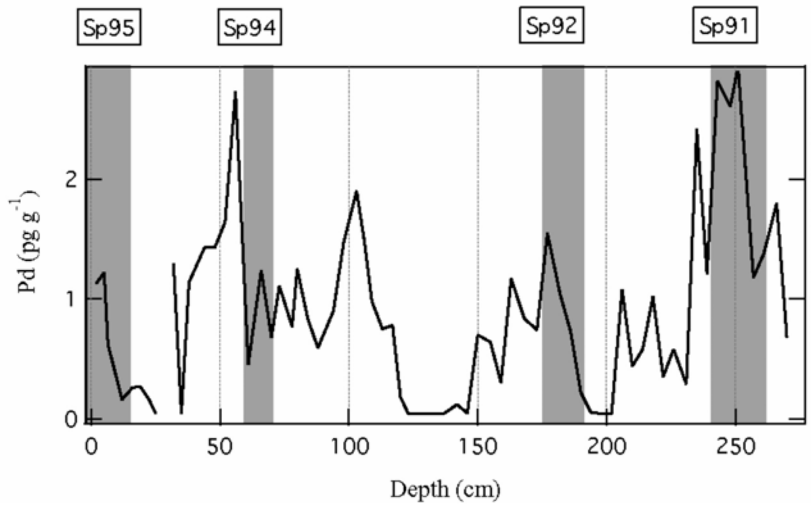

Fig. 3.5.3. Changes in palladium concentrations in Central Greenland snow (Summit) dated from spring 1995 to spring 1991. Vertical grey strips indicate the position of the springs of the years 1995, 1994, 1992 and 1991 as indicated by concentration profiles of calcium and sulphate. Snow depths are shown are the bottom of the figure (surface equal to June 1995). From Barbante and co-workers (Barbante et al. 2003)

Colle Gnifetti (45°54'N, 7°51'E, altitude 4450 m) glacier saddle, located between two summits of Monte Rosa, the second highest mountain (4634 m) in Western Europe, on the Italian-Swiss border. It is probably the location from which the longest Alpine snow and ice time series can be obtained (Döscher et al. 1995). Another site is Col du Dôme, (45°50'N, 6°51'E, altitude 4250 m), a high altitude plateau on the East slope of Dôme de Goûter, about 1.5 km from the summit of Mont Blanc, the highest mountain (4807 m) in Western Europe on the Italian-French border.

Palladium time series have now been obtained both from Colle Gnifetti (Barbante et al. 2004) and from Col du Dôme (Van de Velde et al. 2000). We shall now mainly present the Colle Gnifetti data, since they cover a longer time period than the Col du Dôme data.

The snow and ice samples for Colle Gnifetti were obtained as two cores. The longest core was drilled in 1982 and reached a depth of 109 m (of which only the upper 83 m were analysed for palladium). The second core was drilled in 1995 and reached a depth of 25 m (of which only the upper 13 m were analysed for palladium). Dating shows that altogether the analy-

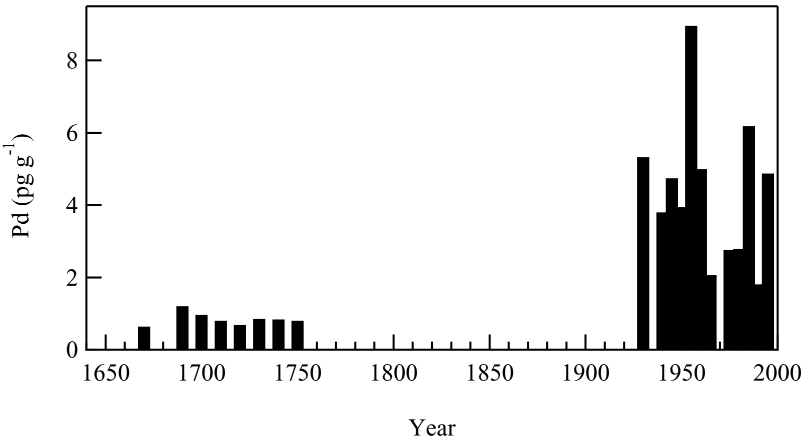

Fig. 3.5.4. Changes in palladium concentrations in snow and ice from Colle Gnifetti, Monte Rosa massif, since the 1650s. The individual data obtained for many depth intervals have been averaged over periods of 5-10 years, giving the bars shown in the figure, allowing to compensate for short term variations and reveals the long time trends. From Barbante and co-workers (Barbante et al. 2004)

sed part of the two cores cover a period of ~ 350 years, from the 1650s to 1994 (with dating uncertainties ranging from ± 2 years for the 20th century to ± 10 years for the oldest samples (Schwikowski et al. 2004)).

Various section of the two cores were analysed for palladium. To isolate the long-term time trends, the individual data points were averaged over periods of 5-10 years to compensate for the observed pronounced short term (intra-annual and inter-annual) variations. The results are illustrated in Fig 3.5.4, which shows changes in palladium concentration from the 1650s to the mid 1990s. They show that palladium concentrations are significantly higher during the 20th century than during the 17th and 18th centuries. As an illustration, the average palladium concentration in snow dated from after 1970 is 3.7 pg g $^{-1}$, which is about 4.2 times higher than the average palladium concentration in ice dated from before 1750. It reflects the increasing contamination of the atmosphere of Western Europe for palladium.

Palladium concentrations measured in Colle Gnifetti snow can be combined with local snow accumulation rates (~ 70 g of water cm^{-2} yr^{-1}) to estimate palladium fallout rates. It gives a fallout rate for recent decades of ~250 pg Pd cm^{-2} yr^{-1}. This is one order of magnitude higher than the corresponding fallout rate at Summit in Central Greenland (~20 pg Pd cm^{-2} yr^{-1}).

Inventories of emissions of metals from anthropogenic sources in Europe over recent decades are available for various metals analysed in the Colle Gnifetti cores (especially Cr, Cu, Zn, Co, Mo, Cd, Sb and Pb (Pacyna 1984; Pacyna and Pacyna 2001)). Unfortunately, these inventories do not include palladium. Interestingly, the Colle Gnifetti data could be used to obtain estimates of palladium emission to the atmosphere from Western Europe around 1980, as follows. The concentrations of the different metals in Colle Gnifetti snow were compared with total emissions from nearby European countries (Italy, Switzerland, Germany, France and Austria), using Zn for normalization. Zn was selected because it is a metal with the highest emissions in Europe around 1980 and it was studied in great detail in the Colle Gnifetti cores. The results show that metal concentrations measured in Colle Gnifetti snow are fairly proportional to the corresponding emissions in Western Europe for the metals for which both concentrations and emission data are available. It is reasonable to assume that the above relationship is valid for other metals such as palladium, which were measured in Colle Gnifetti snow, but for which no emission data are available. It allows us to obtain a tentative emission value of ~ 60 tonnes of Pd per year to the atmosphere from Italy, Switzerland, Germany, France and Austria, at around 1980 (Barbante et al. 2004).

3.5.6 Conclusion

Available data on palladium in polar and Alpine snow and ice archives are still very scarce. The data which have been recently obtain for Greenland and the Alps have however, allowed us to show that palladium concentrations in recent snow are significantly higher than in ancient ice, evidencing a global scale contamination of the atmosphere of the Northern Hemisphere by this metal. It will now be necessary to obtain time series for palladium from the Southern Hemisphere by analysing this metal in dated snow and ice from Antarctica. Also, it will be extremely interesting to obtain comprehensive time series for palladium in Greenland during the post industrial revolution period and during the last decade. Finally, it would be very interesting to investigate past changes in palladium in Greenland and Antarctic ice dated from the last climatic cycles, to better understand the different natural sources of this metal and their changing contributions during glacial and interglacial periods.

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3.6 Palladium in a Mountain Ecosystem (Aspe Valley, Pyrenees, France)

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3.6.1 Introduction

Mobility is one of the most important factors for modern industrial societies in the globalized economy of today. About 90% of the total passenger transport (in passenger per km) and 40% of the freight transport (in tons per km) occurs at the surface, and most of this is powered by fossil fuel combustion engines (Schultz et al., 2004). Road traffic contributes to the deterioration of air quality. The key primary emissions from the transport sector that may have an impact on air quality are: carbon monoxide (CO), hydrocarbons (HC), nitrogen oxides (NO_X), sulphur dioxide (SO_2), particulate matter and air toxics (including organic compounds and metals). Fuel additives, lubricating oils, anti-freeze compounds and the degradation of the different vehicle components are the emission sources of several trace metals into the environment (Dannecher et al., 1990).

Vehicles fitted with catalytic converters significantly minimize undesirable emissions, such as CO, HC, NO_X and particulate matter produced during fossil fuel combustion. Catalytic converters reduce about 90% of these pollutants and transform them into more innocuous carbon dioxide, nitrogen and water. Platinum, palladium and rhodium, known as platinum group elements (PGE), are the active components of catalytic converters. Both platinum and palladium are used to oxidize CO and HC. Rhodium must be present in order to reduce NO_X (Lox and Engler, 1999).

However, due to surface abrasion and deterioration, catalytic converter release PGE into the environment causing their deposition near roads, in vegetation and in other environmental compartments as a result of wind and water transport (Moldovan et al., 2002). A great number of studies have reported the dispersion and accumulation of PGE in numerous environmental matrices. Platinum is the element most studied, while palladium and rhodium have been monitored in more recent research projects. The presence of PGE in urban environments has been fully investigated, but very little research has been performed in rural areas and/or mountain regions.

The Aspe Valley, located in the Pyrenees National Park (Atlantic Pyrenees), is crossed by the RN134 French national road, and due to the low traffic density existing nowadays it could be considered as a pristine area. The opening of the Somport Tunnel, connecting France and Spain, in January 2003 will clear the frontier points of Irún-Biriatou (Atlantic Pyrenees) and La Junquera-Pertuis (Mediterranean Pyrenees) (Etchelecou et al., 2001). On the contrary, the Somport Tunnel will result in a significant increase of road traffic on the Aspe Valley, especially of heavy-duty vehicles, with an expected traffic density of 2000 vehicles per day, and thus it will add a new source of local pollution. Furthermore, the geographical characteristics of the valley together with the atmospheric conditions of the area involve little dispersion of the pollutants and therefore their deposition on the adjacent environment, representing an important impact on the air quality of the valley.

Information concerning air quality in the Pyrenees Mountains is very scarce. During the last two years, a research project has been focussed on the study of the air quality of the Aspe Valley ecosystem and its relation with road traffic (Veschambre et al., 2003). The main objectives of the study were:

- To develop reliable ultra-clean sampling and analytical methods for the determination of trace metals (Al, Ca, Mg, V, Cr, Mn, Cu, Zn, Rb, Cd, Sn, Sb, Ba, Ce and Pb), platinum group elements (Pt, Pd and Rh) and Pb isotope ratios in air particles, bulk wet deposition, snow and epiphytic lichens.
- To study the dispersion of persistent pollutants in the Aspe Valley.
- To evaluate the road transport impact on a mountain ecosystem.

Air particles and bulk wet deposition were monitored for temporal variations, meanwhile fresh snow (short event) and epiphytic lichens (long term study) were used for spatial variations. Within this chapter the presence of palladium in the four sets of environmental samples under study from the Aspe Valley will be presented and discussed.

3.6.2 Sampling sites and sample collection

Air particles and bulk wet deposition samples were monitored during 18 months (from March 2003 to July 2004) at two different sampling stations located in the valley. The first station (Sarrance) was located on the low

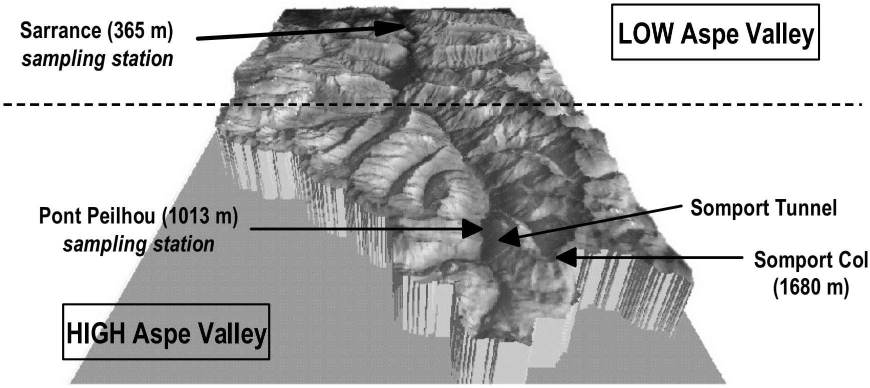


Fig. 3.6.1. Sampling stations location in the Aspe Valley. Picture provided by Prof. André Etchelecou (Université de Pau et des Pays de l'Adour)

valley at 365 m of altitude, and the second one (Pont Peilhou) was situated on the high valley at 1013 m of altitude near to the entrance of the Somport Tunnel (Fig. 3.6.1). Both stations were close to the RN134 road.

Fresh snow was collected after a strong snowing event in March 2004. Epiphytic lichens were sampled during the summer of year 2004. Both snow and lichens were collected along the whole valley at different altitudes and distances from the RN134 road. The selected sampling locations were chosen far from direct anthropogenic sources and sheltered from wind.

Because of the low level of analytes (ng L^{-1} to mg L^{-1}) encountered in the samples under study, ultra-clean conditions were followed during the decontamination of the sampling material and the sampling campaigns. Air particles were collected at a height of 2 meters with respect to the soil. The sampling systems consisted on a polyfluoroalkoxy (PFA) filtration head. The filters, made of Teflon, had a pore size of 0.2 mm and a diameter of 47 mm. The sampling period lasted 15 days, and the average volume of filtered air was 240 m^3. Bulk wet depositions were collected directly in an ultra-trace polypropylene bulk rain sampler during the same period as the air particles. Fresh snow samples were collected (in duplicate) in one litre low density polyethylene (LDPE) bottles. The bottle was driven with ultra clean conditions to the snow pack (19 cm depth). Epiphytic lichens were collected with plastic tweezers from bark trees at 1.5-2 meters height from ground. The following species were identified: *Parmelia sulcata*, *Evernia prunasti*, *Ramalina farinacea*, *Pseudevernia furfuracea*, *Usnea sp*, *Lobaria pulmonaria*, and *Parmelia caperata.*

3.6.3 Sample preparation and analysis

Filters containing air particles and lichens were dried under a laminar flow hood (class 100). Air particles filters were mineralised with a mixture of HNO_3:H_2O_2:HF (6:2:1). Lichens were separated from their substratum, ground in liquid nitrogen, and a fraction of 200 mg was digested with a mixture of *aqua regia*:HF (8:0.5). These solid samples were digested in a microwave oven (Anton Paar, multiwave 3000). Matrix separation procedures were applied in order to minimize interference from the sample matrix. Bulk wet deposition samples were acidified with suprapur HNO_3 (0.5% v/v) and stored at -20°C until analysis. The fresh snow was melted under laminar flow (class 100), acidified with suprapur HNO_3 (0.5% v/v) and frozen (-20°C) until analysis. Analyses were performed by ICP-MS (Thermo X7) equipped with an ultrasonic nebulizer. Interferences were corrected mathematically as reported elsewhere (Moldovan et al., 1999).

3.6.4 Results and Discussion

Air particles

Fig. 3.6.2 shows the palladium content in air particles at both sampling sites during the period March 2003 - February 2004. Palladium, platinum and rhodium were found in all analyzed samples. Pd concentrations were 2 to 6 times higher than Pt ones.

At both sites the determined Pd concentrations were different from the field blanks, which were found to be in the order of the detection limit. At Sarrance the Pd concentration in air particles varied from 0.30 to 4.74 pg m^{-3} (mean value: 1.96 pg m^{-3}), and significantly higher concentrations ranging from 0.77 to 26.87 pg m^{-3} (mean value: 3.96 pg m^{-3}) were determined in the samples collected at Pont Peilhou, especially in sample 18 (26.87 pg m^{-3}) and sample 25 (8.76 pg m^{-3}).

Due to the RN134 road characteristics, the allowed driving speed was similar at both sampling sites, but the mean number of total vehicles per 15 days at Sarrance (3508 vehicles) was almost double than at Pont Peilhou (1548 vehicles) were the road is steep and sharp bended. Furthermore, the record of wind velocity gave mean values of 1.2 and 2.7 m s^{-1} at Sarrance and Pont Peilhou, respectively.

The release of PGE from the catalytic converter surface under real driving conditions is subjected to uncontrolled parameters such related to the catalytic converter, vehicle engine, status and speed of the vehicle, way of

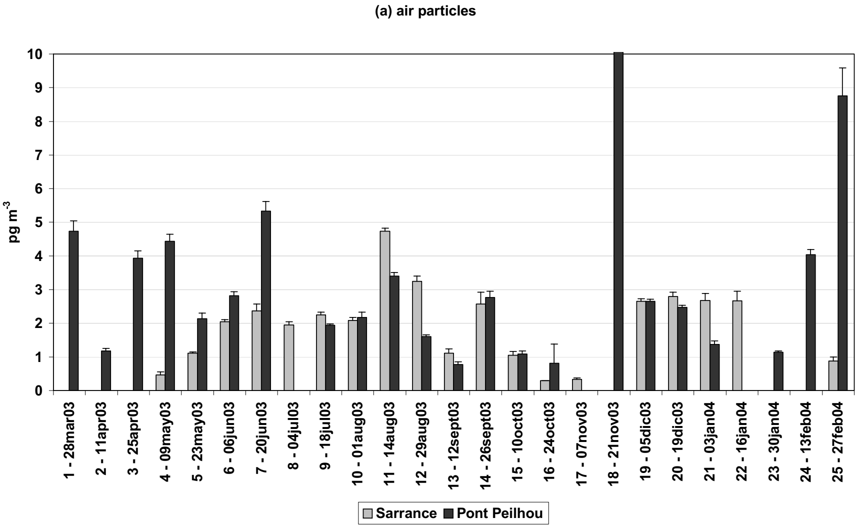


Fig. 3.6.2. Temporal concentration of palladium, expressed in pg m^{-3}, in air particles at Sarrance and Pont Peilhou. On X-axis, the numbers denote the sample number and the sampling day (the end of the 15 days sample collection). The lack of results refers to non-collected samples

driving and meteorological conditions. In the Aspe Valley, catalytic converters are expected to be the most important source for palladium since industrial activities are absent or limited in the area.

Palladium concentrations in airborne from urban areas were reported by several authors (Tilch et al., 2000; Gómez et al., 2002; Limbeck et al., 2004; Zereini et al., 2004), but only few data on Pd concentration in non-urban areas is available. According to Gómez et al. (2002) background values of 5.2 and 3.6 pg m^{-3} were found in Göteborg (Sweden) and Rome (Italy), respectively. The concentration of Pd in total airborne dust (< 22 µm) and in impactor samples (< 10 µm) collected in an area free of traffic close to Frankfurt am Main (Germany) were 2.8 and 7.8 pg m^{-3}, respectively (Zereini et al., 2004). Palladium concentration in air particles from the Aspe Valley is not homogeneous and, as it could be seen in Fig. 3.6.2, shows a temporal variation. In any case, our results lie in the typical range reported in the literature for non-urban areas. The higher Pd presence in air particles at Pont Peilhou could be explained in terms of wind transport, probably from the Aragon Valley (Spain) were the traffic density is higher, especially during the weekends.

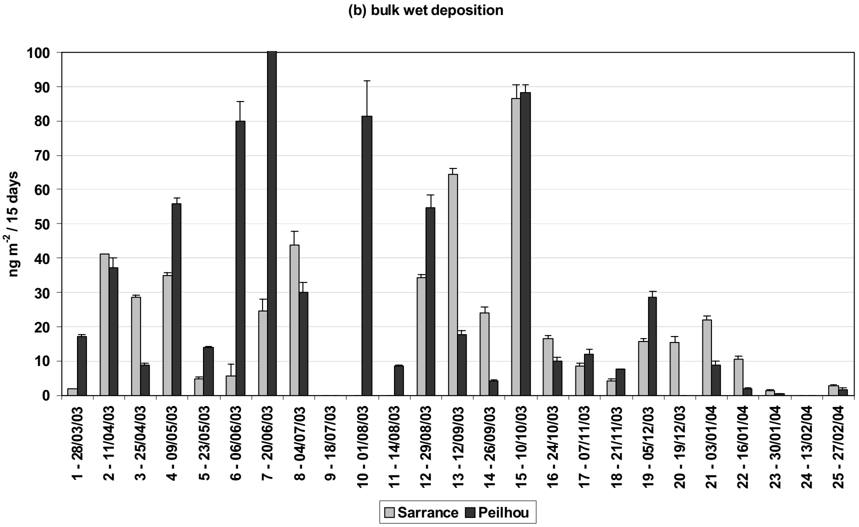


Fig. 3.6.3. Temporal deposition of Pd, expressed in pg m^{-3}, from bulk wet depostion at Sarrance and Pont Peilhou. On X-axis the numbers denote the sample number and the sampling day (after 15 days sample collection). The lack of results means that no samples were collected

Bulk wet deposition

Palladium deposition from bulk wet deposition at both sampling sites during the period March 2003 - February 2004 could be seen in Fig. 3.6.3. Palladium, platinum and rhodium were found in all analyzed samples.

Our sampling device collected bulk deposition, this is rainwater and particles washed out from the local atmosphere, since samples were not filtered before analysis. Rainwater samples presented a pH between 3.7-7.2 at Sarrance, and 3.4-7.3 at Peilhou. The mean amount of rainfall collected was of 50 and 56 mm at Sarrance and Pont Peilhou, respectively.

As it could be observed in the above Figure, the trend of Pd deposition presents a different shape to Pd content in air particles during the 12 months. In general terms, higher Pd deposition corresponds to samples with lower Pd content in air particles, and vice versa. Anyway, Pd depositions were higher at Pont Peilhou (mean value 31.9 ng m^{-2}/15 days, range 0.3 - 228.4 ng m^{-2}/15 days) than at Sarrance (mean value 23.4 ng m^{-2}/15 days, range 1.3 – 86.7 ng m^{-2}/15 days). While at both sites, the Pt/Rh ratios

Table 3.6.1. Summary for concentrations of PGE (expressed in pg g^{-1}) in snow samples from the Aspe Valley. Alpine, Greenland and Antarctic snow PGE concentrations are from Barbante el al., 1999

	Palladium	Platinum	Rhodium
Aspe Valley			
Far from the RN134 road	1.5 ± 0.8	0.6 ± 0.2	0.18 ± 0.04
Close to the RN134 road	7.3 ± 4.5	1.7 ± 0.9	0.3 ± 0.1
Alpine snow	3.6 ± 4.2	0.29 ± 0.62	0.10 ± 0.09
Greenland snow	0.93 ± 0.33	0.37 ± 0.18	0.05 ± 0.03
Antarctic snow	0.54 ± 0.12	0.81 ± 0.36	0.04 ± 0.01

remained constant across the 12 months, the Pd/Pt ratio varied considerably values between 1 and 30. Similar findings were reported by Jarvis et al. (2001).

The content of PGE in bulk wet deposition could be an evidence of: (i) their release from the catalytic converters in a “soluble” form through the exhaust fumes, and (ii) their solubility within the rainwater from a particulate form. According to König et al. (1992), about 10% of the total Pt emissions from catalytic converters are water-soluble. In an engine test bench studies by Artelt et al. (2000), the Pt soluble fraction was approximately 1%. A recent study, reported soluble fractions of 10%, 40% and 40% for Pt, Pd and Rh, respectively in car exhaust fumes (Moldovan et al., 2002). This implies that the effects of Pd and Rh emissions could have a more adverse effect on the environment than Pt emissions. On the other hand, the solubility of PGE depends on particle size and the pH, as shown by Nachtigall et al. (1996).

Fresh snow

The presence of the three PGE has been observed in Antarctic snow and ice as reported by Barbante el al. (1999). A large fraction of the Pt and Rh fraction found in the Greenland snow and ice could originate from catalytic converters, while for Pd this last contribution could not be detected (Barbante el al., 2001).

The Pd, Pt and Rh content was measured in 13 fresh snow samples collected at different locations within the Aspe Valley, at locations far and close from the RN134 road, as summarized in Table 3.6.1. As it could be observed, our results are in the same concentration range than those already published. Samples collected in Greenland and Antarctica indicates that there is a global spreading of the PGE. The content of PGE in samples from the Alps and the Pyrenees present a similar trend, this is higher Pd concentration compared to the Pt and Rh ones.

Epiphytic lichens

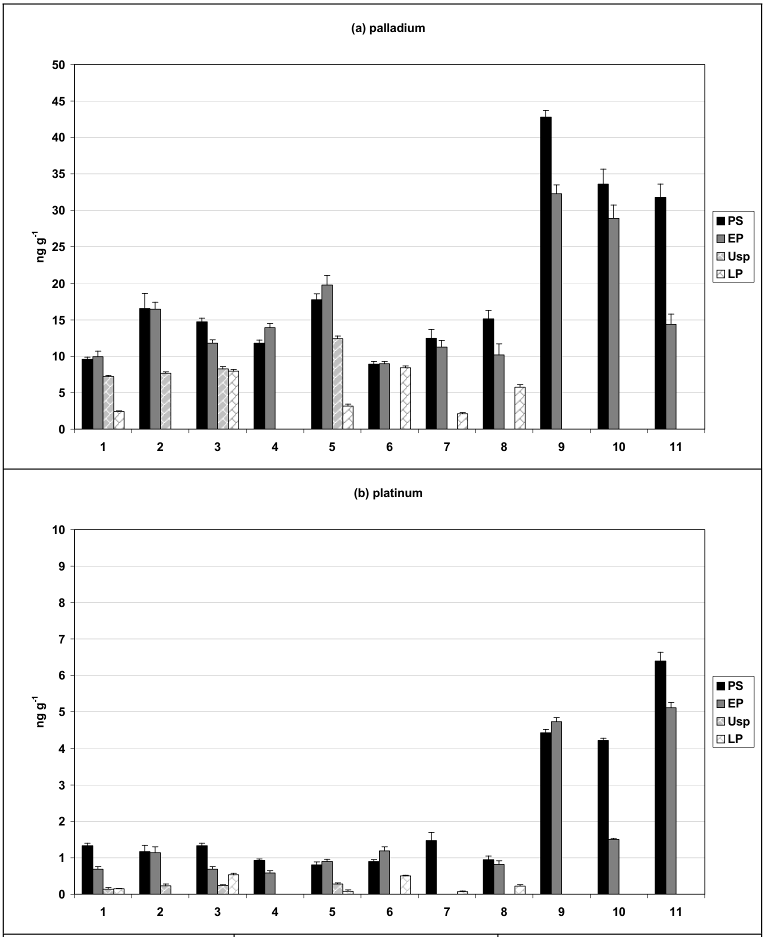
The analysis of plants exposed to high-traffic density shows that the concentration of PGE exceeds the natural background levels, and therefore most of the studies have been involved in the sampling of vegetation adjacent to the heavily travelled highways. Analytical results of these environmental samples have shown an upward trend of PGE concentrations over time and a strong impact of the traffic conditions. However, in several reports of the roadside vegetation, the data do not necessarily represent the real PGE uptake, rather the dust deposition, collection and adsorption on the external surface of roadside plants.

Nowadays, lichens are becoming an attractive indicator of air pollution. Epiphytic lichens are useful in atmospheric deposition studies where the integration of long-term signals requires monitoring. Due to the lack of absorbing roots, epiphytic lichens have a major dependence on atmospheric sources of nutrients (Conti and Cecchetti, 2001). As a consequence, epiphytic lichens have often been used as surrogate receptors for atmospheric deposition of metals, radionuclides, and organic pollutants.

Palladium, platinum and rhodium were found in the analyzed samples, although Rh was present at lower level compared to the other two elements. Fig. 3.6.4 present the content in Pd (Fig. 3.6.4a) and Pt (Fig. 3.6.4b) in *Parmelia sulcata*, *Evernia prunasti*, *Usnea sp*, and *Lobaria pulmonaria.*

Eleven locations have been selected, from which sites 1-3 correspond to areas far from the RN134 road, sites 4-8 correspond to locations more than 200 m away from the main road, meanwhile sites 9-11 are located close (< 5 m) to road RN134. *Parmelia sulcata* and *Evernia prunasti* have been collected at all sampling sites, meanwhile *Usnea sp* and *Lobaria pulmonaria* were found only on the sites far from the road, since these lichen species are more characteristic of non-polluted areas.

From Fig. 3.6.4, we can conclude that: (i) Pd and Pt were present in all samples; (ii) both elements presented at higher content in samples collected close to the road; (iii) Pd concentration was higher than Pt one in the four lichen species; and (iv) for both elements a higher concentration was observed *Parmelia sulcata* and *Evernia prunasti* compared to *Usnea sp* and *Lobaria pulmonaria*



Background	**> 200 m to RN134 road**	**close to RN134 road**
1. Espelunguere 2. Chemin Belonce 3. Castet de Bergout	4. Peyrenere 5. Montengou 6. Borde de Mirande 7. Pont Peilhou 8. Chemin de la Mature	9. Entrance tunnel 10. Entrance Etsaut 11. Entrance CetteEygun

Fig. 3.6.4. Palladium (Fig. 3.6.4a) and platinum (Fig. 3.6.4b) concentration (expressed in ng g^{-1}) in *Parmelia sulcata* (PS), *Evernia prunasti* (EP), *Usnea sp* (Usp), and *Lobaria pulmonaria* (LP) at different locations in the Aspe Valley

Very little is known on the uptake of traffic related PGE by the terrestrial biosphere. In the field studies, elevated and continuously increasing Pt and Pd levels were described for roadside grass samples (Helmers and Mergel, 1997; Hees et al., 1998; Schuster et al., 2000). Greenhouse experiments showed that various plant species grown in soils doped with PGE present a soil-plant transfer in the order of Pd>PtRh (Schafer et al., 1998). Therefore, Pd is the most biologically available in this group.

Lichens are not dependent of soil-plant transfer. Nevertheless, the accumulated elements could reproduce the atmospheric deposition signature. Furthermore, the accumulation could be linked to the biological characteristics of the lichen specie. Up to now, the use of lichens as PGE biomonitors is very scarce. Zschau et al. (2003) reported concentrations of 0.07 ± 0.04 $\mu g\ g^{-1}$ of Pd and 0.21 ± 0.15 of Pt $\mu g\ g^{-1}$ in the epilithic lichen *Xanthoparmelia* collected in Maricopa Country (Arizona) during 1998. These results, although in a similar concentration range, present different Pd/Pt ratio compared to our findings. The higher Pd content in rainfall could explain the higher concentration of this element in the studied lichen species.

3.6.5 Conclusions

The present research represents the first systematic study focussed on the presence of Pt, Pd and Rh in a mountain valley. The occurrence of PGE in the four types of samples has been detected, and in all samples Pd was the PGE that showed higher concentration. Vehicles fitted with Pd-containing catalytic converters are considered the main source for Pd emissions, and their number is continuously increasing.. The metallic form of palladium may be inert as far as biological reactions are concerned, but this is not the case of the bioavailable fraction. The toxic effect of palladium for living organisms and humans is still under discussion

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3.7 Short-Term Variation of Palladium in Airborne Particulate Matter

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3.7.1 Introduction

Platinum group elements (PGEs) can be naturally found only at very low concentration in the earth crust, a situation which is changing with the release of PGEs from automobile catalysts. Platinum (Pt), rhodium (Rh), and palladium (Pd) are used in motor vehicle exhaust systems to catalyze the conversion of hydrocarbons, carbon monoxide, and nitrogen oxides into the less harmful substances carbon dioxide, nitrogen, and water. With the use of automobile catalytic converters fine particulate material originating from the abrasion and the deterioration of the surfaces of the catalysts is introduced in the environment (Wei and Morrison 1994; Moldovan et al. 1999). They are emitted mostly as abraded wash coat particles with a size range from sub-micrometer to several micrometers (Gomez et al. 2001; Zereini et al. 2001) with emission rates in the ng km^{-1} range (Moldovan et al. 1999; Palacios et al. 2000). As a result a clear link between the use of automobile catalytic converters and increasing concentrations of PGE in the environment has been observed, especially in traffic exposed environmental samples like road dust, soils or adjacent vegetation (Schäfer et al. 1999; Jarvis et al. 2001; Zereini et al. 2001).

Platinum is the element that has received the most attention among the PGEs studies, while Pd and Rh have been monitored in more recent research projects. Recently it has been demonstrated that Pd has a greater mobility in the environment than either Pt or Rh (Moldovan et al. 2001), which means that Pd undergoes environmental transformations into more reactive species which may be bioavailable (Schäfer et al. 1998; Rauch and Morrison 2000; Moldovan et al. 2001; Philippeit and Angerer 2001). Therefore it becomes more important to investigate Pd levels in the environment. Although palladium concentrations have been determined in different environmental samples such as road dust, soils or vegetation (Jarvis et al. 2001; Müller and Heumann 2000; Schäfer et al. 1999) information about the atmospheric occurrence is very sparse. Limited sample amounts combined with numerous interferences in the most sensitive analytical techniques are considered to be the major difficulties. However, several techniques have been applied to the determination of palladium traces in airborne particulate matter including electro thermal atomic absorption spectrometry (Limbeck et al. 2003), electro thermal atomization laser excited atomic fluorescence spectrometry (Tilch et al. 2000) and inductively coupled plasma mass spectrometry (Rauch et al. 2001; Petrucci et al. 2000) in particular in combination with isotope dilution mass spectrometry (Kanitsar et al. 2003). However, in all of the mentioned studies the described results were derived from very limited sample sets disabling the determination of temporal trends.

Data about long-term observations of PGE concentrations in airborne particulate matter, which are necessary to define average concentrations, are reported for Pt and Rh only. Zereini et al. (2001) observed a 46-fold enhancement in the Pt levels of air over a 10-year period (from 1988 to 1998), whereas the Rh concentration increased by a factor of 27. These results indicate a trend toward continuous increases in ambient concentrations of these metals between 1988 and 1998. Based on the growing demand for palladium in the last years (Matthey 2001) a similar increase of the palladium content in airborne dust could be expected. Schäfer et al. (1999) have shown that the short-term variation of PGE concentrations and their ratios in airborne dust were due to wind and rain. These findings were confirmed by Limbeck et al. (2004), who reported a complete annual cycle for the palladium concentration in airborne particulate matter, indicating that the seasonal variation of the palladium concentration is caused by changes in the meteorological conditions. However, these studies were based on the investigation of monthly collected aerosol samples and provide therefore no information about the daily variation of the palladium concentration in airborne particulate matter. To assess the risks associated with the emission of palladium into the environment additional data on ambient concentrations is needed; in particular investigations with shorter sampling intervals (days instead of weeks or months) are required.

In this work aerosol samples collected at three different sites in Vienna, Austria were analysed to determine the short-term variation of palladium in the atmospheric aerosol. Based on the determined palladium concentrations and the results obtained for the aerosol mass the palladium content of the aerosol samples was calculated. The results obtained for the three investigated sites were compared and the differences observed between the individual sampling sites are discussed.

3.7.2 Experimental

Sample collection

Ambient aerosol samples were collected at three different sites in Vienna, Austria. One sampling site was located at the Institute of Chemical Technologies and Analytics in downtown Vienna (Getreidemarkt). The air quality at this site is strongly influenced by traffic emissions since it is surrounded by several major streets. The sampling location was situated approximately 20 m away from a heavy frequented road with 6 lanes. During the day the driving conditions at this site are affected by stop and go traffic, whereas in the night free cruising conditions are predominant. A second set of aerosol samples was collected close to the Danube river bank in Kaisermühlen, which represents a site with very low traffic intensity. The sampling location was placed at the outlet of the fire fume ventilation of the Kaisermühlen tunnel. The Reichsbrücke, which crosses the Danube and connects this outer part of Vienna with the City, is the closest major road with a distance of approximately 500 m to the sampling site. Although there are some narrow roads which connect Kaisermühlen with the Tunnel and the Reichsbrücke the contribution of local traffic emissions to the air quality is expected to be negligible at this site. Thus the concentration and composition of airborne particulate matter at this site is more affected by meteorology and emissions of the surroundings. The third sampling site (Hietzing) was situated at the western access road of Vienna which connects the end of the A1 highway with the city of Vienna. With few exceptions free cruising conditions are the main driving conditions at this site. The sampling device at this site was operated next to the street and was exposed to emissions from only one direction. Nevertheless a great impact of the local traffic emissions could be expected, since aerosol samples were collected very close to the street – between the sampling site and the road was only a small pedestrian walkway. The location of the three sampling sites is presented in Fig. 3.7.1.

At all three sites open-face-sampling was performed with a low volume sampler (flow rate about 35 L min^{-1}). Sampling substrates were mixed cellulose ester filter (Pall GN-4 Metricel membrane filter, 47 mm Ø). At each site the sampling head with the filter facing downwards was situated under a shelter, which was mounted on a pole with the open side down. Considering the used sampling flow rate this polyethylene shelter leads to an upper cut-off diameter for aerosol particles of 30 µm. The sampling volumes were measured with mechanical gas meters and converted to standard temperature and pressure (273 K, 1013 hPa). At the sites Getreidemarkt and Kaiser-

Fig. 3.7.1. Map of Vienna indicating the sampling locations

mühlen aerosol samples have been collected for two days (48h) or three days (72h) corresponding to sampling volumes in the range of 90–145 m³. Sample changes were performed from approximately 10:00 to 10:30 a.m. every second respectively third day. Sample changes in Hietzing were conducted between 8:30 and 9:00 a.m. every day. The air volumes collected within approximately 24 hours varied between 43 and 47 m³. After sampling, the filters were stored in petri dishes at room temperature. To exclude any contamination from the sampling procedure itself, field blanks were collected by purging ambient air for 30 s through the filter.

Sample preparation and analysis

To determine the collected aerosol mass each sample was weighed on a microbalance (Sartorius M5P-000V001) after 2 h equilibration at constant temperature (20°C) and humidity (50%). Sample filters were weighed before and after sampling, the observed mass difference was attributed to the amount of sampled particulate matter.

The palladium content of the collected aerosol samples was analyzed using a flow injection procedure with ETAAS detection for the on-line matrix separation and pre-concentration of palladium in environmental samples (Limbeck et al. 2003). The developed method involves a two step digestion procedure for the complete mineralization of the collected aerosol including the sampling substrate, which allows an interference free determination of palladium in the solution derived after sample digestion. In a first step each sample was digested with 3 mL concentrated nitric acid in a closed PTFE vessel at 180°C. To volatilise probably existing siliceous material and to dissolve remaining elemental carbon the digestion procedure was followed by an open vessel treatment with 500 µL concentrated HF and 250 µL concentrated $HClO_4$. The use of $HClO_4$ was observed to be advantageous, since compared to evaporation steps with HNO_3, the temperature of the reaction mixture could be increased, improving the HF attack on silicates, ensuring the dissolution of precipitates, and facilitating the complete removal of HF (Totland et al. 1995). Moreover, $HClO_4$ enabled a complete oxidation of elemental carbon and organic material. After evaporation of the volatile acids the obtained liquid residue consisting of $HClO_4$ and dissolved metals was diluted with 5 ml 0.6 mol L^{-1} HCl.

The selective enrichment of palladium was performed using the recently presented technique for the determination of palladium in airborne particulate matter (Limbeck et al. 2003). The prepared sample solution was purged by an argon stream through a C18 micro column that has been reversibly loaded with the complexing agent N,N-diethyl-N´-benzoyl-thiourea (DEBT). Due to their specific class (b) properties noble metal ions were selectively retained on the micro column (Schuster 1992), whereas sample constituents which did not react with the complexing agent passed through the column. After complex formation a wash step with HCl was performed to remove the residual matrix from the column. Finally the column was dried by an argon air stream. For elution of the formed palladium complex and the excess ligand the eluent solution (about 150 µL ethanol partitioned into several segments with argon bubbles) was pumped through the column in reverse direction to the loading of the analyte. The first segments of the eluate (approximately 50 µL) were directly introduced into the graphite furnace of a Perkin-Elmer 4100 ZL Zeeman atomic absorption spectrometer. Quantification of the palladium content was based on a calibration - function which has been determined with palladium standard solutions for the complete procedure. The standard solutions were prepared just before use by appropriate dilution of a stock solution with 0.6 mol L^{-1} HCl. The complexing agent was prepared from benzoyl-isothiocyanate and aminoethanol and recrystallized with ethanol (Douglas and Dains 1934). With the use of a

1.57 ml sample loop detection limits in the order of ~ 25 ng L^{-1} (varied from day to day) and quantification limits of approximately 40 ng L^{-1} were obtained, with a relative standard deviation being not more than 3.9%. The accuracy and the applicability of the developed procedure were evaluated by the analysis of the certified reference material BCR-723.

3.7.3 Results

Overall Results

The aerosol mass concentrations determined at the three investigated sites were in the order of several µg m^{-3}. At the sampling site in Hietzing the particulate matter concentrations varied between 41.4 and 104.3 µg m^{-3}, for Kaisermühlen values ranging from 25.2 to 92.6 µg m^{-3} were determined. Lowest aerosol mass concentrations varying from 22.0 to 51.8 µg m^{-3} were achieved at the site in downtown Vienna (Getreidemarkt). The concentrations observed at all three sites were in the typical range reported for urban samples. Typically PM concentrations vary from a few µg m^{-3} in moderately polluted environments to tens of µg m^{-3} in heavily polluted environments under unfavourable meteorological conditions (Stedman 2002; Querol et al. 2001; Röösli et al. 2001; Harrison et al. 1997).

Palladium was present in all samples with concentrations above the quantification limit (around 1.9 pg m^{-3}). At all three sampling sites the determined palladium concentrations were distinctly different from the field blanks, which were found to be in the order of the detection limit (around 1.5 pg m^{-3}). In Kaisermühlen the palladium concentration varied from 2.0 to 8.6 pg m^{-3}. Significantly higher concentrations ranging from 3.2 to 13.0 pg m^{-3} were determined at the Getreidemarkt in Downtown Vienna. The Pd concentration at the sampling site in Hietzing varied between 5.2 and 12.5 pg m^{-3}. Table 3.7.1 presents a compilation of the results achieved for palladium and aerosol mass concentrations.

For the sampling sites located in the vicinity of major roads the release of platinum group elements from auto-catalytic converters is expected to be the most important source for the occurrence of palladium in airborne particulate matter, since in the neighbourhood of these sampling sites industrial activities such as mining, smelting, chemical industry and municipal waste incineration are absent or very limited. Since the site in Kaisermühlen is relatively free of traffic, the observed palladium concentrations could only partially explained with local PGE emissions. Thus an additional source must be considered – transport of PGE containing aerosol par-

Table 3.7.1. Ambient aerosol mass and palladium concentrations

	Getreidemarkt		Kaisermühlen		Hietzing	
Sampling period	21.01.-25.02.2002		18.09.-08.10.2002		07.04.-26.04.2003	
Sampling intervals	48 -72 h		48 h		24 h	
Collected samples	15		10		15	
	Pd [pg m^{-3}]	PM [µg m^{-3}]	Pd [pg m^{-3}]	PM [µg m^{-3}]	Pd [pg m^{-3}]	PM [µg m^{-3}]
Minimum	3.2	22.0	2.0	25.2	5.2	41.4
Maximum	13.0	51.8	8.6	92.6	12.5	104.3
Average	7.3	36.1	4.8	52.8	9.2	72.2
Median	6.8	34.5	4.1	48.9	9.7	73.3

ticles from emission sites to non-urban or background areas leading to a widespread distribution of PGE in airborne particulate matter. The prevailing wind directions in Kaisermühlen are along the Danube valley with comparable frequencies for westerly and easterly flows. Thus air masses from the northwest and the southeast of Vienna could be transported to the sampling location enhancing the local PGE concentrations in Kaisermühlen.

The palladium concentrations observed at the three sites are in good agreement with the results reported for other European Cities. For a suburb of Berlin palladium concentrations of <0.2 to 14.6 pg m^{-3} were reported (Tilch et al. 2000), whereas extremely high concentrations ranging from 21.2 to 85.7 pg m^{-3} were found in Rome (Petrucci et al. 2000). Varga et al. (2003) reported Pd concentration ranges of 0 - 370 pg m^{-3} for a high traffic site in Mestre Venice. For size segregated PM10 samples from the urban air of Göteborg palladium concentrations ranging from 0.1 to 10 pg m^{-3} were found (Rauch et al. 2001). Elevated values of 5.1 to 32 pg m^{-3} were reported for a highway in Madrid (Gomez et al. 2003). For different sampling sites in Frankfurt airborne palladium concentrations ranging from <0.5 to 44.3 pg m^{-3} were reported (Zereini et al. 2004).

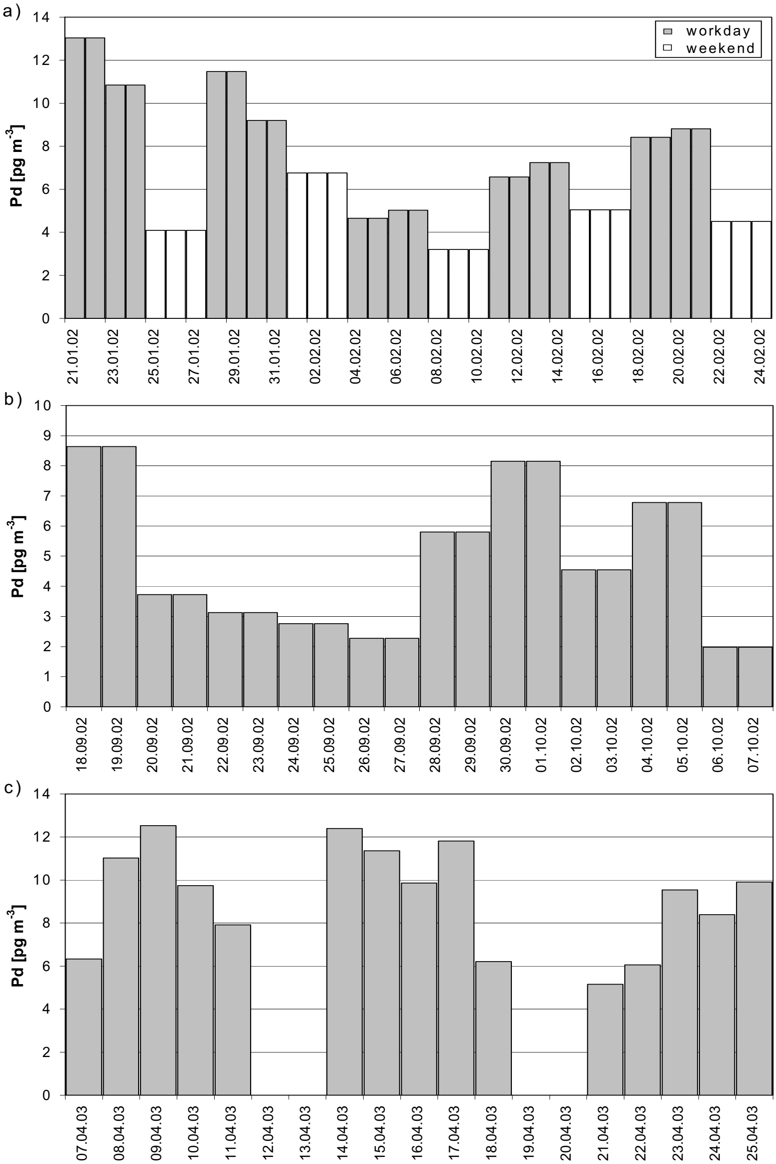

Fig. 3.7.2. Variation of the palladium concentration in airborne particulate matter:
a) Getreidemarkt, b) Kaisermühlen and c) Hietzing

Short-term variation

The variation of the palladium concentrations at the three sampling sites is depicted in Fig. 3.7.2. The palladium concentration ranges observed at the three sites were similar, although the sampling intervals at the site in Hietzing were distinctly shorter than at Kaisermühlen and Getreidemarkt. Between the lowest and the highest concentration at each site factors in the order of 2.4 to 4.4 were achieved. At all three sites the highest palladium concentrations were in maximum 1.8 times higher than the corresponding mean. Summing up at all three sites minor variations in the palladium concentrations were determined, but rigorous changes in the palladium concentration were not observed. This result contradicts the findings of Zereini et al. (2004), who reported heterogeneous Pd concentrations in airborne particles collected at three different sites in Frankfurt. In some samples they found palladium concentrations that were considerably higher than in the remaining airborne dust samples. For example at the sampling site located at the edge of a little frequented street a mean palladium concentration (n=20) of 6.0 pg m^{-3} was determined, but in one sample an enhanced value of 38.9 pg m^{-3} was observed. Such isolated cases of high concentrations have already been described previously. Rauch et al. (2001) reported for aerosol samples collected in the City of Göteborg concentrations in the lower pg m^{-3} range, but two samples presented significantly higher concentrations which were not caused by any errors or interferences in analysis. The observed results were explained with the presence of relatively few particles with high PGE concentrations. Thus the amount of palladium accumulated on the filter substrate during sampling is influenced by the collection of one or more PGE containing particles.

The palladium concentration showed no significant time trend in Hietzing and Kaisermühlen, respectively. A different result was observed at the sampling site Getreidemarkt in Downtown Vienna. Highest palladium concentrations occurred during the working days, whereas lower amounts were determined at the weekends. This result could be explained with the changing traffic density. At the weekends the traffic intensity decreased, which causes reduced palladium emissions for these days. During the working days conditions with heavy traffic were predominant, leading to enhanced palladium concentrations. Lowest concentration levels were observed during the winter-holidays (4th of February to 11th of February 2002), which were assumed to be a result of the reduced traffic intensity at this time of the sampling period. These results confirm the known correlation between ambient PGE concentrations and the traffic intensity (Gomez et al. 2000; Rauch et al. 2001; Zereini et al. 2001).

During sample collection the meteorological conditions (e.g. wind direction, rain or snow fall) changed considerably. However, at all three sites the palladium concentration levels showed no remarkable dependence from these changes, although the meteorological conditions are known to be important parameters by which analyte concentrations in airborne particulate matter are influenced. This observation could be explained with the relatively large intervals used for sample collection (24 to 72 h), which were possibly too long to see the influence of the meteorological conditions, since variation of e.g. wind direction and speed occurs in much shorter periods.

3.7.4 Discussion

PGE concentrations in airborne particulate matter are influenced by a variety of different parameters e.g. the traffic density, the driving conditions, the traffic composition and the meteorological conditions (Artelt et al. 1999; Gomez et al. 2001; Zereini et al. 2001), therefore it is not surprising that the palladium concentrations observed at the three sampling sites are different. As the sampling technique used for aerosol collection was the same at each sampling location, it could be assumed that the observed differences in the Pd concentrations are mainly caused by differences in the meteorological conditions (i.e., wind and rain), the traffic intensity and the driving conditions.

Considering these parameters lowest palladium concentrations could be expected for the sampling site in Kaisermühlen, since this site is relatively free of traffic. Enhanced palladium levels were assumed for the two sites in the vicinity of major roads with heavy traffic. At both traffic sites PGE concentrations originate from local traffic emissions which add to the regional background level. Highest concentrations were expected for the site in Downtown Vienna, since this sampling location is surrounded by several streets with heavy traffic intensity, whereas the site in Hietzing is exposed to traffic emissions from less cars and one direction only. In addition it has to be considered that the driving conditions predominant at the Getreidemarkt (stop and go traffic) lead to increased PGE emissions, while for free cruising conditions, which are the principal driving conditions at the site in Hietzing, reduced emission rates for PGE were reported (Artelt et al. 1999).

On average, the palladium concentrations decrease from the site in Hietzing to the sampling location in Kaisermühlen (see Table 3.7.1). The lowest mean palladium concentration was observed at the sampling station which is relatively free of traffic, but surprisingly, the site in Hietzing showed the highest mean palladium concentration. This unexpected result indicates that the palladium concentrations at the investigated sites are influenced not only by traffic – other factors which might influence ambient PGE concentrations had to be considered. They are influenced by a variety of different factors which must be accounted for to allow comparisons between different sampling locations. The meteorological conditions, the traffic density (Gomez et al. 2000; Rauch et al. 2001) and the driving conditions (Artelt et al. 1999) are known to be the most important parameters by which PGE concentrations in airborne particulate matter are influenced. Differences in traffic intensity and driving conditions could be excluded for explaining the observed result, because the assumption of higher palladium levels at the sampling site Getreide-markt was based on differences in these parameters. Thus differences in the meteorological conditions (e.g. wind direction, wind speed, rainfall) might be responsible for the unexpected results at the heavy traffic sites, although the palladium levels at the individual sites showed no significant dependence from these parameters. Following Hazenkamp-von Arx et al. (2003) local traffic emissions become rather unimportant when the sampling sites are off-road by 150 m and more, but the situation changes considerably when the aerosol is sampled in traffic. Since the sampling site in Hietzing was located directly beside the street more or less undiluted traffic emissions were collected, whereas at the Getreidemarkt the sampling device was operated in a distance of approximately 20 m to the road, which causes the collection of diluted traffic emissions only. Thus differences in the atmospheric dilution of emitted PGE, which affect the ambient PGE levels, were assumed to be responsible for the observed results. The same explanation could be used to account for the higher aerosol mass concentrations in Hietzing.

The influence of atmospheric dilution could be eliminated by determining the palladium content of the collected aerosol particles. In contrast to particulate matter or individual analyte concentrations the aerosol composition did not change significantly during the short time required for the transport from the surrounding streets to the sampling device. Based on the determined palladium concentrations and the results obtained for the aerosol mass the palladium content of the aerosol samples was calculated (Table 3.7.2). At the sampling site in Kaisermühlen an averaged concentration (n=10) of 98.1 ng g^{-1} was achieved, whereas for Hietzing (n=15) a distinctly higher palladium load of the aerosol was observed (148.3 ng g^{-1}). The highest mean palladium content (n=15) was determined at the Getreidemarkt in Downtown Vienna (189.4 ng g^{-1}). These results are in good agreement with the traffic intensities observed at the three sites. Comparing these findings with literature data for other environmental samples different

Table 3.7.2. Palladium content of the aerosol samples

	Getreidemarkt	Kaisermühlen	Hietzing
	Pd-content [ng g^{-1}]	Pd-content [ng g^{-1}]	Pd-content [ng g^{-1}]
Minimum	132.4	48.4	79.1
Maximum	297.6	199.1	206.7
Average	195.2	98.1	130.6
Median	190.7	90.0	121.4

results were achieved. For road tunnel dust comparable results in the order of several hundred ng g^{-1} were reported (Petrucci et al. 2000; Boch et al. 2002), and similar results were observed for sewage sludge incineration ashes (Schäfer et al. 1999), while the palladium content of road dust, tunnel dust and soil samples is in the lower ng g^{-1} range (Schramel et al. 2000; Müller and Heumann 2000; Köllensperger et al. 2000; Sures et al. 2001). Lowest palladium contents ranging from <0.3 to 2 ng g-1 were determined in vegetation adjacent to major roads like trees (Helmers 1997) or grass (Schuster et al. 2000).

3.7.5 Conclusions

In this study aerosol samples from different sites in Vienna, Austria were analysed to determine the short-term variation of palladium in the atmospheric aerosol. The observed palladium concentrations varied between 2.0 and 13.0 pg m^{-3} which agrees with findings reported for other European Cities. Between the lowest and the highest concentration at each site factors in the order of 2.4 to 4.4 were achieved, indicating that during sample collection only minor variations in the palladium concentrations occurred. Interpreting the derived results it was found that the atmospheric dilution of traffic emissions during transport from the emission site to the sampling site is the most important parameter by which ambient palladium concentrations are influenced. To reduce the effect of atmospheric dilution the determination of the palladium content in airborne particulate matter is recommended, since only the particle concentration and not the particle composition is affected by short transport processes. Based on the determined palladium concentrations and the results obtained for the aerosol mass the palladium content of the aerosol samples was calculated, which ranged from 48.4 to 297.6 ng g^{-1}. In contrast to the palladium concentrations were the results for the palladium contents in good agreement with the traffic intensities observed at the investigated sites.

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3.8 Palladium in Airborne Particulate Matter: Total Concentrations and Particle Size Distribution

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3.8.1 Introduction

Catalytic converters were introduced in Europe in the mid-1980's to reduce hydrocarbon, carbon monoxide and nitrous oxide emissions in automobile exhausts. Emission reductions are achieved with the use of the catalysts platinum (Pt), rhodium (Rh) and palladium (Pd), noble metals which are often referred to as platinum group elements (PGE). Platinum is used in the greatest amounts in Pt-Rh catalytic converters at a ratio of 5.1. Previous studies of airborne particulate matter have tended to focus on Pt, as this element has dominated PGE emissions from catalytic converters. Since 1993, however, Pd has been increasingly used in place of Pt at levels as much as 5 g per catalyst litter volume Pd. The total amount of Pd used in the catalytic converter industry has increased significantly in recent years, from 3.6 tonnes in 1993 to 39.8 tonnes in 2003. This represents an 11-fold increase in the consumption of this element over a 10 year period (Johnson Matthey Platinum 1996, 2004).

Only a few data have been published so far on Pd concentrations in airborne particulate matter. In their analysis of air samples collected in Berlin in 1997, Tilch et al. (2000) found that airborne Pd concentrations ranged from 0.2 to 14.6 pg/m^3. Palladium concentrations in samples collected in Göteborg in 1999 were reported to vary between 0.1 to 10 pg/m^3 (Rauch et al. 2001). In Rome, average Pd concentrations in samples of airborne particulate matter were 37.2 and 69.5 pg/m^3 in the years 1998 and 1999, respectively (Petrucci et al. 2000). Palladium concentrations were about 3 to 6 times higher than those found for Pt in this study. Airborne concentrations of Pd in samples collected in Salzburg in 2001 were reported to range from 7.1 to 31.2 pg/m^3 and had an average content of 16.5 pg/m^3 (Limbeck et al. 2004). Automobile catalytic converters are clearly a primary contributor to increased levels of PGE in the atmosphere. These metals are released in small amounts as a result of elevated temperatures and vibration of the catalytic material in the converter. Platinum group element emissions have led to elevated levels of these elements in the environment (see Alt et al. 1993; Schierl 2000; Zereini et al. 2001; Gomez et al. 2000, 2001; Rauch et al. 2001; Kanitsar et al. 2003, Zereini et al. 2004, 2005).

The goal of this study was to investigate the concentration, particle size distribution and spatial dispersion of heavy metals, including Pd, in total and fractionated airborne dust (diameter range from > 9 µm to < 0.43 µm). This was conducted as part of a project of the Hessisches Landesamt für Umwelt und Geologie. Some of the results presented have been published elsewhere (see Zereini et al. 2004; Zereini et al. 2005).

3.8.2 Sampling

Airborne dust samples were collected at three locations with different traffic densities in the Frankfurt am Main area in Germany. Site 1 was a main street with a traffic load of 32 500 cars/day, while site 2 was a side street with < 1 000 cars/day. Site 3 was located in a large garden area on a hill (elevation 165 m) about 8 km NW of the city centre. This latter site is relatively free of traffic and can be considered a rural area for the purposes of this study. Total and fractioned airborne dust samples were collected simultaneously at the three locations. Varying degrees of contamination, as well as meteorological aspects, were considered in the selection of sampling sites.

The total airborne dust samples with an aerodynamic equivalent diameter of < 22 µm were collected on cellulose nitrate filters (Sartorius, pore diameter: 3 µm; filter diameter: 120 mm) via air filtration devices (LIS-P devices). The samples were taken approximately every 19 days from August 2001 to July 2002. The sampling time per filter was 24 h. The sampled air volume was between 310 and 350 m^3. Eight-stage Andersen impactors with an aerodynamic equivalent diameter of < 10 µm were used to determine heavy metal concentrations in various airborne dust fractions (particle diameters of between >9, 9.0-5.8, 5.8-4.7, 4.7-3.3, 3.3-2.1, 2.1-1.1, 1.1-0.63, 0.63-0.43, and <0.43 µm). Samples were collected directly on glass disks in the impactor. Cellulose nitrate filters (Sartorius, pore diameter: 3 µm) were used as the backup filter.

At each location, three impactor samples were collected over a period of about 30 days at intervals of 2 - 3 months. A sampling flow rate of 28.3 L/ min was used and the sampled volume varied between 1140 and 1215 m^3. Samples were taken at a height of about 4 m above the ground.

3.8.3 Analytical Methods

Samples were placed in quartz glass vessels in an autoclave and digested with an acid mixture of 4 mL of 14M HNO_3 and 0.5 mL of 12M HCl in a high pressure asher (HPA, Küner, Rosenheim, Germany) at 320 °C and a maximum of 130 bar (Alt et al. 1993, Hoppstock & Alt 2000). The HPA digestion solution was treated with about 2 mL of 40% HF in a Teflon dish and then washed several times with HNO_3. The solution was subsequently evaporated down to a few microliters. After cooling, the solution was filled up to 10 mL with deionized water.

Palladium was measured using total reflection X-ray fluorescence analysis (TXRF) (R. Seifert & Co, Ahrensburg, Germany). Prior to analysis, 3 ml of the HPA digestion solution were placed in a quartz glass container. After addition of 200 µl Hg (II) nitrate solution (30 mg Hg) and 2 x 500 µl formic acid, the vessel was heated in a metal block to about 80 °C for approximately 30 min. The temperature was then increased to about 120 °C for another 10 min. During this procedure, a Hg drop forms on the bottom of the container, in which Pd and Au are enriched. The solution was subsequently filtered and the residue rinsed several times with water. The Hg drop was then heated for 15 min at approximately 300 °C on a hydrophobic TXRF carrier on a hot plate to evaporate the Hg. A detailed description of the analytical procedure can be found in the work of Messerschmidt et al. (2000).

The detection limit for a sample of 400 mg of airborne dust was calculated to be 170 pg/g Pd. The digestion blank value was < 20 pg (abs.) and the recovery rate was > 93%, with a standard deviation of ±5%.

3.8.4 Results and Discussion

Concentration of Palladium in Total Airborne Dust

The results for Pd in total airborne dust from the three sampling sites are displayed in Table 3.8.1 and Fig. 3.8.1. The concentration of Pd in samples collected at the main street sampling site was 14.7 pg/m^3 and ranged between < 0.6 and 44.3 pg/m^3. Samples from the side street contained 3.5

Table 3.8.1. Palladium concentrations in total airborne dust and impactor samples (pg/m^3) (average values (min/max values)). (permission from Zereini et al., 2004, copyright American Chemical Society)

Location	Size Fraction	Palladium	Samples
Main Street	PM < 22 µm (LIS-P Sampler)	14.7 (<0.6 – 44.3)	20
	PM < 10 µm (Impactor)	25.1 (9.4 – 29.3)	3 Impctors
Side Street	PM < 22 µm (LIS-P Sampler	3.5 (<0.6 – 7.8)	20
	PM < 10 µm (Impactor)	8.9 (5.1 – 15.6)	3 Impctors
Rural Area	PM < 22 µm (LIS-P Sampler)	2.8 (<0.5 – 11.2)	20
	PM < 10 µm (Impactor)	7.8 (4.7 – 11.7)	2 Impctors

pg Pd /m^3 on average. Palladium concentrations ranged from < 0.6 to 7.8 pg/m^3 for this site. For samples from the rural area, Pd concentrations were 2.8 pg/m^3 on average and varied between < 0.5 und 11.2 pg/m^3. These concentrations are comparable to those measured for air samples collected in Salzburg, Austria (Limbeck et al. 2004).

In addition to Pd, Pt and Rh were measured in samples of airborne dust. Platinum occurred in the highest concentrations, followed by Pd and Rh. Palladium occurred in higher amounts in some samples, however, which is a likely result of particle abrasion from the catalyst surface. Platinum con-

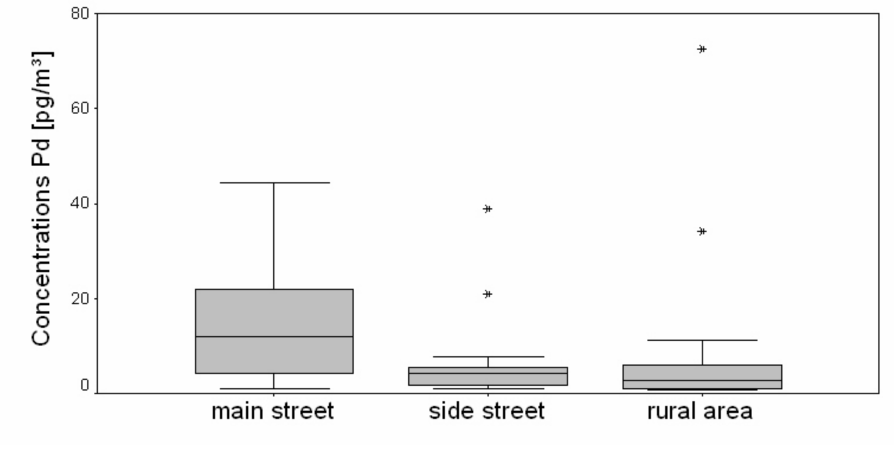

Fig. 3.8.1. Distribution of Pd concentrations in air (in pg/m^3) * outliers

centrations were 23 pg/m^3 and ranged between 2.4 and 55.4 pg/m^3. Samples contained significantly less rhodium, with an average of 3.9 pg/m^3. Concentrations ranged between <0.5 and 11.6 pg/m^3 for this metal.

On average, Pd concentrations at the sampling sites strongly decreased in the following order: main street > side street > rural area (Fig. 3.8.1). The results show a clear relationship between airborne Pd concentration and traffic density. The highest Pd concentrations occurred in air near the main street sampling site, which has a traffic load of approximately 32 500 motor vehicles/day. At the side street site, where the traffic load is only 500 to 1000 motor vehicles/day, the airborne concentration of Pd is far lower. It is lowest at the rural site, which is relatively traffic-free. Similar observations have been made for Pt and Rh concentrations in airborne particulate matter (Zereini et al. 2004).

Palladium measured in samples collected in the low-traffic rural area NE of Frankfurt likely originates from the city, being transported as aerosols by the prevailing south-westerly wind in this region. However, automobile catalytic converters cannot be assumed to be the only source of elevated PGE levels in the environment. Other emission sources such as the chemical industry, primary PGE deposits and platinum-processing industries also contribute to the widespread distribution of PGE in the atmosphere (Boyd et al. 1997).

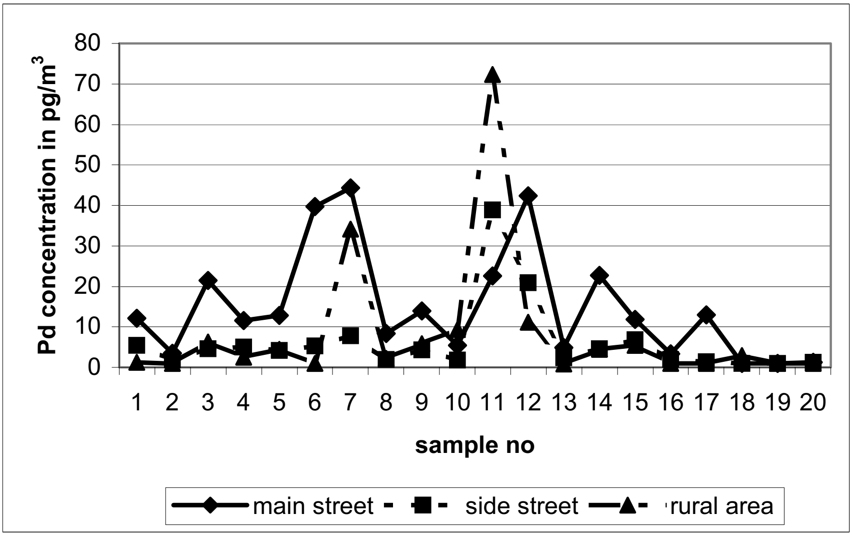

Fig. 3.8.2. Distribution of Pd concentrations (in pg/m^3) in air during the sampling period from August 2001 (sample no. 1) to July 2002 (sample no. 20) (sampling time about every 19 days)

In this study, palladium concentrations in airborne particulate matter varied throughout the year at all three sampling sites (Fig. 3.8.2). Concentration patterns between sites were also found to be highly variable over the course of the sampling year. This heterogeneity in concentrations is likely due to climatic factors such as wind and precipitation. In particular, wind direction seems to strongly influence concentrations, as indicated by the occurrence of fluctuations in metal amounts measured for each site in conjunction with changes in wind direction (Fig. 3.8.2).

Two airborne dust samples from the side street site exhibited unusually high Pd concentrations of 20.9 and 38.9 pg/m^3. Similarly, two samples from the rural site had elevated Pd concentrations of 34.0 and 72.0 pg/m^3 (Fig. 3.8.1). Elevated concentrations were also observed for some of the fractionated air dust samples. Although these samples appear to be outliers, they are likely due to what has been termed the "nugget effect". This is a result of particulate emissions from catalytic converters due to the abrasion of catalytic materials. As indicated by the fact that these samples do not contain equivalent high concentrations of Pt and Rh, PGE are not always emitted in similar amounts from catalytic converters. This may also be a reason for the high variability observed in Pt/Rh and Pd/Rh ratios in airborne dust (Zereini et al. 2004).

Concentration of Palladium in Fractionated Airborne Dust

To determine the particle size distribution of airborne dust and its metal concentrations, samples were collected using an 8-stage Anderson impactor equipped with a backup filter. Sampled particle size fractions had an aerodynamic equivalent diameter of between >9, 9.0-5.8, 5.8-4.7, 4.7-3.3, 3.3-2.1, 2.1-1.1, 1.1-0.63, 0.63-0.43 and <0.43 µm.

Similar to total airborne dust samples, average Pd concentrations were the highest in fractions from the main street site and declined rapidly to the side street and rural sampling locations. In contrast to the total airborne dust samples, Pd occurred in the highest amounts in fractionated samples from all three locations, followed by Pt and Rh.(Zereini et al. 2004). This indicates that Pd is primarily present in fine airborne particles with a diameter < 10 µm. This would explain why this metal is more water soluble than Pt and Rh (Jarvis et al. 2001), as fine particles tend to have a higher solubility compared to coarse particles.

Palladium concentrations of the impactor samples collected at each site varied in terms of particle size. There were also differences between sampling locations in terms of this metal's association with certain particle size

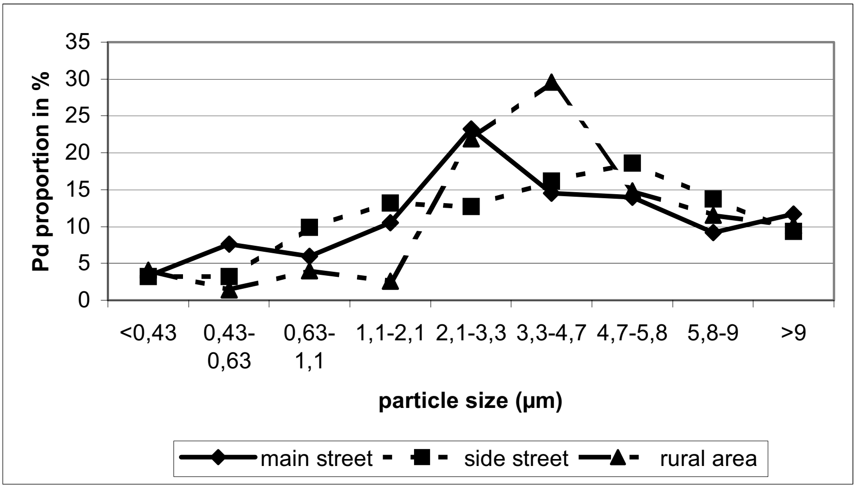

Fig. 3.8.3. Distribution of Pd in fractionated airborne dust (proportion in % , average values from 3 impactors per site, collection time 30 days per impactor)

fractions. Generally, the concentration of Pd in fine dust (< 2.1 µm) was less than that measured in coarse dust particles (> 2.1 µm). The same was also observed for Pt and Rh (Zereini et la. 2004).

At the main street sampling site, the particle size fraction 2.1 – 3.3 µm displayed the highest Pd concentrations (Fig. 3.8.3). This represents 23% of the total Pd present in fractionated airborne dust. Palladium was also present in the impactor samples with a similar particle size. Concentrations strongly declined with a decrease in particle size. Fine dust particles with a diameter of < 0.63 µm contained the lowest Pd concentrations, with about 7% of the total Pd present in fractionated samples. At the side street site, dust particles with a diameter of 4.7 – 5.8 µm exhibited the highest concentrations of this metal. In samples collected at the rural location, the highest concentrations of palladium occurred in particles with a diameter between 3.3 and 4.7 µm (Fig. 3.8.3).

On average, the concentration of Pd in total airborne dust with an aerodynamic equivalent diameter < 22 µm from all three sampling sites was lower compared to fractionated samples with a diameter of < 10 µm (Tab. 3.8.1). For all sampling locations, airborne dust particles with a size of > 2.1 µm contained the greatest amount of Pd.

Knowledge regarding Pd concentrations in the various size fractions is crucial in assessing the potential risks of exposure to this metal. The depth to which contaminants may penetrate the human lung and elicit a toxic effect is a function of particle size. Specifically, particles less than 10 µm in diameter are deposited in the bronchial tree, while particles smaller than 3 µm can reach the alveolar tract of the lungs. Particularly these smaller particles are of toxicological concern.

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3.9 Source Characterization of Platinum Group Elements Using the Isotopic Composition of Osmium

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Environmental studies on platinum group elements (PGE) have mostly focused on platinum, palladium and rhodium owing to their use in automobile catalysts and their emission into the environment (Palacios et al., 2000). Fewer studies have dealt with the environmental relevance of the other PGE, i.e. iridium, ruthenium and osmium (Muller et al., 2000; Ely et al., 2001; Fritsche et al., 2004; Rauch et al., 2004a). Elevated Os concentrations compared with expected background have recently been reported in environmental samples and Os isotopic composition proved to be useful for source characterization (Esser et al., 1993; Ravizza et al., 1996; Williams et al., 1997; Helz et al., 2000; Rauch et al., 2004a, 2004b). Here we review the current knowledge on Os in the environment and propose an approach for PGE source characterisation using Os isotopic composition.

3.9.1 Determination of Os concentration and isotopic composition

Low environmental concentrations are a major obstacle to the accurate of determination of Os concentration and isotopic composition, which require sensitive analytical techniques such as secondary ion mass spectrometry (SIMS) (Esser et al., 1993), negative thermal ionization mass spectrometry (N-TIMS) (Ravizza et al., 1996; Helz et al., 2000) and inductively coupled plasma-mass spectrometry (ICP-MS) (Hassler et al., 2000; Rauch et al., 2004a, 2004b) combined with preconcentration and interference separation or correction procedures. Although N-TIMS offers higher precision for isotope ratio measurements, ICP-MS is increasingly used as it provides higher sample throughput at sufficient precision for environmental Os isotope studies, even with a single detector, owing to the large variation in isotopic composition (over one order of magnitude).

A number of sample preparation procedures has been developed to isolate and concentrate Os. The case study presented here is based on single collector ICP-MS analysis after preparation by NiS fire assay. The NiS bead is dissolved and residual insoluble PGE-containing phases retained on a cellulose filter that is dissolved in hot concentrated acid. This treatment also oxidises Os to volatile OsO_4 that is introduced into the plasma with the Ar stream. Platinum, Pd, Ir, Ru and Rh were analysed in the remaining solution. Quantification was performed by isotope dilution for Pt, Pd, Ir and Os. Rhodium was quantified by first normalizing Rh count rates to Pt and Pd counts rates and secondly by converting normalized count rates to concentrations using Pt and Pd concentrations obtained by isotope dilution. Further details are provided by Rauch et al. (2004a,b) and Hassler et al. (2000).

3.9.2 Sources of Os into the environment

Osmium occurs naturally at trace concentrations with 31 pg g^{-1} estimated for the Earth's upper continental crust (Peucker-Ehrenbrink et al., 2001). For comparison, Pt, Pd, Ir and Rh have upper crustal concentrations of 510 pg g^{-1}, 520 pg g^{-1}, 21 pg g^{-1} (Peucker-Ehrenbrink et al., 2001) and 60 pg g^{-1} (Wedepohl, 1995), respectively.

Elevated Os concentrations have recently been measured in the environment (Table 3.9.1). Osmium has a limited number of uses and therefore potential sources are limited. Medical and research laboratories account for about 80 % of osmium use, the largest single use being as fixative and stain for the preparation of thin sections for electron microscopy. Osmium is also used by chemical and electrical industries (Esser et al., 1993).

Secondary pollution by the use of chemicals with Os present as impurity has also been discussed. Sediment records are suggestive of Os release by Cr tanning as a results of high Os concentrations in mafic minerals from which commercial Cr is mined (Rauch et al., 2004a). In addition, the occurrence of elevated Os concentrations in the roadside environment has been related to Pt/Pd/Rh-based automobile catalysts (Fritsche et al., 2004; Rauch et al., 2004a).

Table 3.9.1. Osmium concentration and $^{187}Os/^{188}Os$ in background and contaminated samples.

Sample	Location	Concentration (pg g^{-1})	$^{187}Os/^{188}Os$	Ref. [a]
Background samples				
Upper Continental Crust	-	0.03	1.40	1
Eroding Continental Crust	-	-	1.05	1
Coastal sediments	Long Island Sound	0.04	1.04-1.08	2
Coastal sediments	Massachusetts	0.02-0.11	0.972-1.093	3
Lake sediments	Upper Mystic Lake	0.06-0.16	1.92-2.21	4
Soil	Austria	0.04-0.09	-	5
Contaminated samples				
Coastal sediments	Long Island Sound and New Haven Harbor	0.06-0.77	0.22-0.60	2
Coastal sediments	Boston Harbor	0.29	0.354	3
Coastal sediments[b]	Long island Sound	0.06-0.13	0.613-0.689	6
Lake sediments[c]	Upper Mystic Lake	0.19-0.40	0.361-0.685	4
Lake sediments[d]	Upper Mystic Lake	0.09-0.15	0.651-1.177	4
Sewage sludge	New Haven	0.57	0.18	2
Sewage sludge	Boston	1.31-4.01	0.15-0.17	3
Roadside soil	Austria	<0.004-2.36	-	5
Tunnel dust	Austria	1.21	0.271	4

[a] References in the table: (1) Peucker-Ehrenbrink et al., 2001; (2) Esser et al., 1993; (3) Ravizza et al., 1996; (4) Rauch et al., 2004a; (5) Fritsche et al., 2004; (6) Williams et al., 1997;

[b] Sediments at location A;

[c] Layer corresponding to Cr contamination by tanning industries; [c] Top of sediment core corresponding to 1999-2002

Elevated Os concentrations have been reported in sewage sludge and sewage has therefore been considered as an important environmental pathway for Os contamination from industrial and laboratory uses (Ravizza et al., 1996). Automobile emission may lead to a much more widespread contamination due to transport by both airborne particles and stormwater (Rauch et al., 2004a, 2004b).

3.9.3 The isotopic composition of osmium

Due to the production of ^{187}Os by the $^{-}$-decay of ^{187}Re (half life of ~42 Gyr, Smoliar et al., 1996) the isotopic composition of Os in a sample under close-system conditions depends on its initial ^{187}Os/^{188}Os, its Re/Os concentration ratio and its age. The high ^{187}Os/^{188}Os of ~1.40 for the continental crust reflects its old age and relatively high Re/Os compared to the Earth's mantle (Peucker-Ehrenbrink et al., 2001). Loess, a proxy for the eroding continental crust, has a ^{187}Os/^{188}Os of 1.05 ± 0.23 (Peucker-Ehrenbrink et al., 2001).

Esser and co-workers (1993) were the first to report that commercial Os has a distinctive isotopic composition because it is mined from mantle-derived PGE deposits with a low Re/Os concentration ratio and, consequently, a low ^{187}Os/^{188}Os of ~0.1-0.2 (Esser et al., 1993). Isotopic composition has supported the conclusion that anthropogenic Os emission into the environment is occurring (Esser et al., 1993; Ravizza et al., 1996; Williams et al., 1997; Helz et al., 2000). A low ^{187}Os/^{188}Os of 0.271 has been reported for tunnel dust with an elevated Os concentration and indicates that the Os emitted from catalysts with an isotopic composition similar to that of mantle-derived Os (Rauch et al., 2004a).

3.9.4 PGE source characterization

Elevated PGE concentrations in the urban and roadside environment have been attributed to emission from automobile catalysts with source characterization based on (1) the knowledge of potential sources, (2) decreasing PGE concentrations with increasing distance from roads, (3) correlation with traffic density and (4) similarity of the environmental PGE concentration ratios with the ratio in catalysts. However, concentrations do not always correlate with traffic density due to external parameters affecting PGE emission and deposition. Similarly, the use of PGE ratio is flawed by the wide range of catalyst compositions. Contributions from natural and anthropogenic PGE sources have been estimated by the calculation of enrichment factors, but conclusions may be affected by a number of factors including local variations in crustal composition and biogeochemical differences between the element of interest and the reference element (Reimann et al., 2000).

Here, we propose here an alternative approach that enables the estimation of natural and anthropogenic contributions to PGE concentrations in a sample using Os isotopic composition. The estimation of anthropogenic and natural contributions is especially important in remote environments where concentrations are lower than in the urban environment.

The anthropogenic fraction of Os (AF_{Os}) is estimated using the measured Os isotopic composition and reasonable estimates for natural and anthropogenic Os isotopic composition (Equation 1). Small differences in the atomic weight of the end members can be neglected in the mass balance calculations because they do significantly affect the results (for details see Peucker-Ehrenbrink, 1996).

$$AF_{Os} = \frac{({}^{187}Os/{}^{188}Os)_{natural} - ({}^{187}Os/{}^{188}Os)_{sample}}{({}^{187}Os/{}^{188}Os)_{natural} - ({}^{187}Os/{}^{188}Os)_{anthropogenic}} \tag{1}$$

The natural component describes all Os from non-anthropogenic sources and is therefore assigned the isotopic composition of the eroding continental crust, i.e. $^{187}Os/^{188}Os$ of 1.05 ± 0.23 (Peucker-Ehrenbrink et al., 2001). To include potential local variability in natural and anthropogenic isotopic compositions, ranges of values were computed. Natural and anthropogenic isotopic composition were considered to be in the range 0.82-1.28 (99.5% confidence interval) (Peucker-Ehrenbrink et al., 2001) and 0.1-0.2 (Esser et al., 1993), respectively.

Natural and anthropogenic Os concentrations can then be estimated using Equations 2 and 3.

$$[Os]_{anthropogenic} = [Os]_{sample} \times AF_{Os} \tag{2}$$

$$[Os]_{natural} = [Os]_{sample} \times (1 - AF_{Os}) \tag{3}$$

Finally, natural and anthropogenic PGE contributions can be estimated from the relative PGE concentrations using Os concentration in the natural contributors and assuming that the natural contributors have the same relative composition as the Upper Continental Crust (UCC) (Equations 4 and 5, presented for Pd). Crustal PGE composition has been provided by Peucker-Ehrenbrink and Jahn (2001) for Ir, Os, Pd, Pd and Ru, and Wedepohl (1995) for Rh.

$$[Pd]_{anthropogenic} = [Pd]_{sample} - \frac{[Pd]_{UCC}}{[Os]_{UCC}} \times [Os]_{natural} \tag{4}$$

$$[Pd]_{natural} = \frac{[Pd]_{UCC}}{[Os]_{UCC}} \times [Os]_{natural} \tag{5}$$

Potential shortcomings of the method include local deviations in natural Os isotopic composition and relative PGE concentrations from the global average, and differential mobility of PGE in the environment. The determination of AF_{Os} solely depends on Os isotopic composition and is therefore not affected by differential mobilities. Sources of error in the quantification of natural and anthropogenic concentrations for other PGE include local variations in the relative PGE composition. Due to the biogeochemical similarities of PGE, this source of error likely smaller than that incurred in the commonly used determination of the anthropogenic fraction of an element using a lithogenic tracer.

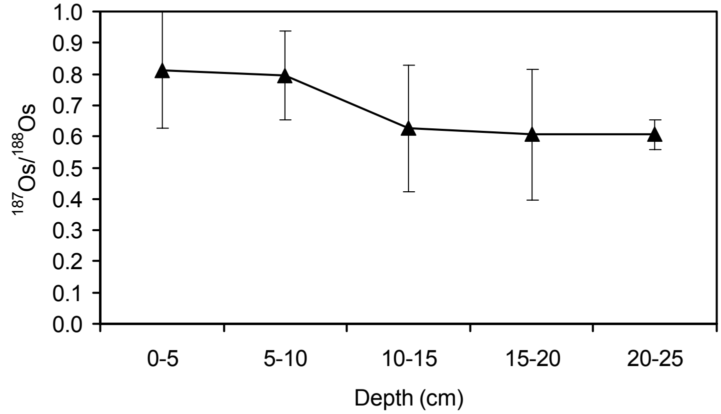

Fig. 3.9.1. Average Os isotopic composition profile in peat from Thoreau's Bog. Vertical bars represent 1σ uncertainties

3.9.5 Example of an ombrotrophic peat bog

The source characterisation approach presented here was applied to the study of PGE in Thoreau's Bog, an ombrotrophic peatbog in Concord, Massachusetts, USA. Ombrotrophic peatbogs receive minerals by atmospheric deposition only and therefore, the determination of PGE in peat from Thoreau's Bog can provide information relevant to the occurrence of PGE in atmospheric particles.

Osmium, Ir, Pd, Pt and Rh concentrations and Os isotopic composition ($^{187}Os/^{188}Os$) were obtained in a set of 21 samples from 2 independent cores collected at Thoreau's Bog in 2002. Osmium, Ir, Pd, Pt and Rh concentrations in Thoreau's Bog were found to be elevated compared with expected concentrations estimated using a lithogenic tracer, with enrichment factors of 25, 129, 191, 694 and 496, respectively (Rauch et al., 2004b). The average osmium isotopic composition in the bog is relatively low with an average $^{187}Os/^{188}Os$ of 0.612±0.189, providing evidence for anthropogenic Os input (Rauch et al., 2004b). The relatively large variation in $^{187}Os/^{188}Os$ is the result of both between-core and between-sample variability. As a result of this high variability, the apparent difference between the top 10 cm and below 10 cm is not statistically significant, but indicates the occurrence of two different layers.

The anthropogenic fraction of Os was estimated using Equation 1. Because Os isotopic composition in a sample results from the mixing of natural and anthropogenic Os, the isotopic composition of Os in any sample should be intermediate between the two end members. While this constraint does not affect the range estimated for anthropogenic Os isotopic composition, the range in natural Os isotopic composition was corrected to 1.07-1.28 for Thoreau's Bog to account for the apparently slightly more radiogenic nature of the local background. Using minima and maxima for both natural and anthropogenic Os isotopic compositions, four AF_{Os} values were obtained for each sample and averaged. The residual standard deviation for the four values is less than 20% in most samples, with the exception of samples with a more radiogenic isotopic composition, i.e. $^{187}Os/^{188}Os > 0.8$. The average anthropogenic Os contribution ranges from 9% to 88%. The large variation indicates a large variability in the source of Os and is probably the results of heterogeneously distributed anthropogenic and natural Os. The anthropogenic Os fraction profile indicates the occurrence of two section in the bog, with the top 10 cm having a higher relative natural Os input, although the difference is not significant owing to large variation in individual samples (Fig. 3.9.2). The difference is however supported by correlation between Os concentration and anthropogenic os fraction (Fig. 3.9.3).

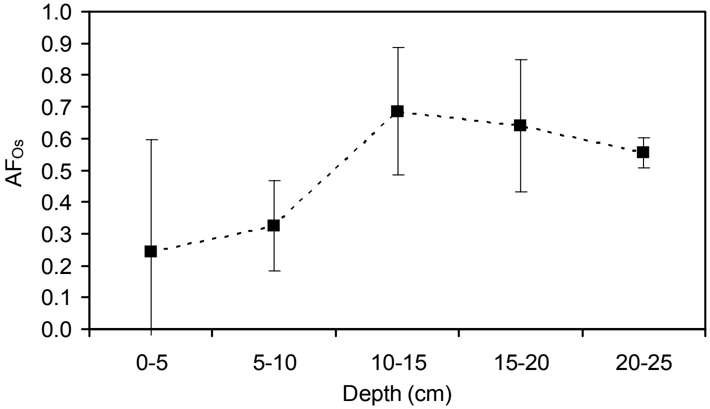

Fig. 3.9.2. Anthropogenic fraction of Os in peat cores from Thoreau's Bog

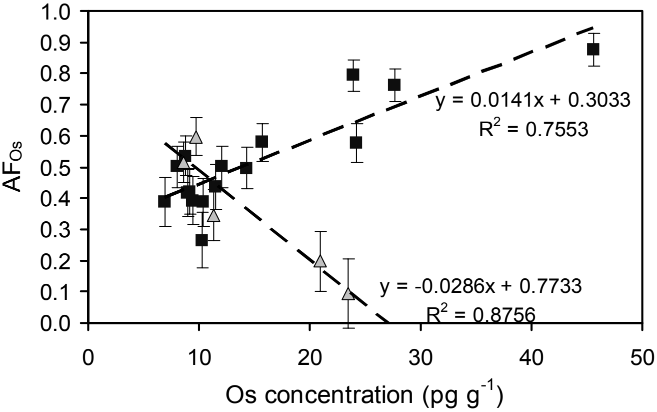

Fig. 3.9.3. Correlation between the anthropogenic fraction of Os, with 1 standard deviation error bars, and total Os concentrations for the top 8 cm (triangles) and below 8 cm (squares) in Thoreau's Bog

For samples below 8 cm, higher Os concentration corresponds to a larger anthropogenic Os input (and a lower $^{187}Os/^{188}Os$). In contrast, in the top 8 cm, higher Os concentrations correspond to a relatively higher natural Os input. The top 8 cm of the peat cores are dominated by vegetation and therefore, this contrast may reflect preferential incorporation of natural Os into plant matter.

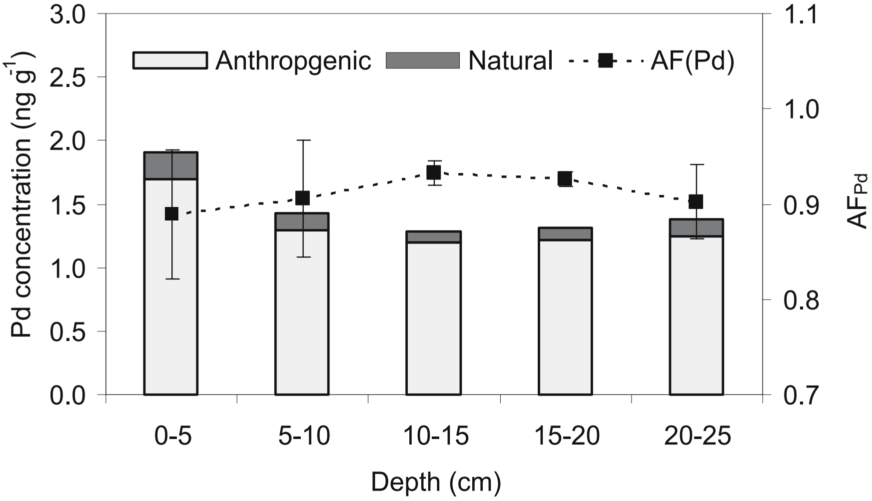

Fig. 3.9.4. Average anthropogenic and natural Pd concentrations, and the anthropogenic fraction of Pd in peat cores from Thoreau's Bog

The anthropogenic fractions of Pd, Pt, Rh and Ir (estimated from Equations 4 and 5) are found to represent 80-95%, 93-100% 91-99% and 66-96% of total concentrations, respectively. Therefore, the results provide evidence that PGE from an anthropogenic source are transported to Thoreau's Bog. Automobile traffic is the only known source of PGE in the vicinity of the bog, with the nearest roads at approximately 300 m from the bog. The occurrence of anthropogenic PGE in Thoreau's Bog therefore indicates regional atmospheric transport of PGE from automobile catalysts. Changes in Pd concentration in peat cores are presented in Fig. 3.9.4. Palladium concentration is higher at the top of the peat core due to increase in both natural and anthropogenic Pd. Natural Pd deposition is expected to be relatively constant over the time scale represented by the peat cores (25 cm correspond to approx. 25 years of accumulation, Rauch et al. 2004b) and therefore, the higher natural Pd concentration may be the result of preferential Pd accumulation into plant matter. It is possible that increase in anthropogenic PGE at the top of the core is also caused by preferential accumulation into plant matter, although an increase in anthropogenic Pd input cannot be ruled out.

Comparison of natural PGE concentrations with lithogenic concentrations estimated using Al as a lithogenic tracer (Rauch et al., 2004b) indicates the occurrence of a non-lithogenic source of natural Os. Rain has been sug-

Table 3.9.2. Average PGE concentrations and contributions from different sources in Thoreau's Bog (Rauch et al., 2004b)

Sample	PGE concentration (ng g^{-1})			
	Total	Lithogenic	Rain-derived	Anthropogenic
Os	0.0015	0.0004	0.0006	0.0005
Ir	0.05	0.0003	0.01	0.04
Pt	5.0	0.007	0.1	4.9
Pd	1.4	0.007	0.1	1.3
Rh	0.42	0.0009	0.02	0.40

gested a source of Os into the bog and is believed to be an important sources of Os, but a relatively minor source of Pt, Pd and Rh owing to their predominantly anthropogenic origin. The contribution of lithogenic sources, rain and anthropogenic sources are presented in Table 3.9.2.

3.9.6 Conclusion

Osmium isotopic composition is a powerful indicator of the source of Os in the environment. Rather than depending on other, chemically much more different, lithogenic tracers, the Os isotopic composition can be used as an alternative means of estimating sources of complementary PGE. The method presented here was applied to PGE source characterisation in an ombrotrophic peat bog and demonstrated the occurrence of Os from both natural and anthropogenic origin. Palladium, Pt, Rh and Ir in the bog are predominantly anthropogenic. Automobile catalysts are the only known, viable source of PGE in the vicinity of the bog. Regional atmospheric transport of PGE from automobile catalysts is therefore indicated.

Acknowledgement

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3.10 Temporal and Spatial Variation of Palladium in the Roadside Environment

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3.10.1 Introduction

Studies on the behaviour of the PGE emitted from automobiles have historically focussed on platinum, due to the fact that it has dominated the three way catalyst since it became compulsory in Europe in 1993. However, increasing sales of cars utilising the palladium-rich catalyst, has resulted in renewed interest in this element and its fate in the environment. Although potentially as important in the environment as Pt, Pd has not been studied as widely because of problems perceived to be associated with the analytical methodology for this element. Inductively coupled plasma-mass spectrometry (ICP-MS) is now the most commonly used technique for the study of anthropogenic PGE. It is extremely sensitive (lower limit of detection = 0.025 µg/kg) and provides data for Pt, Pd and Rh simultaneously. In the past researchers have reported less reproducible results for Pd in environmental samples than Pt or Rh. For example, Pt:Rh ratios tend to be rather constant while Pt:Pd ratios are variable. Some authors have suggested that this variability is due to analytical imprecision, rather than to any process taking place after deposition on the road surface. However, it has been shown that ICP-MS combined with a fire assay pre-concentration step can provide very high quality data (Jarvis et al. 2001) confirming that observed variation is actually due to the different behaviour of Pd in the environment, compared to the other PGEs.

It is important to carry out systematic studies in order to build up a picture of how the PGE are deposited and distributed in the roadside environment. This must be done both temporally and spatially before any accurate statement can be made regarding typical behaviour of the PGE. There has been limited work reported on the ultimate fate of the PGE once deposited at the roadside. Although Pt and Rh have low solubility in soils and surface waters (Zereini et al. 1997), it has been demonstrated that finely divided Pt can dissolve in biogenic substances (Freislenen et al. 1993). It has been shown that natural complexing agents such as humic acid in soil will increase the solubility of Pt (Lustig et al. 1998; Lustig et al. 1996) and that

Pt and Rh from catalytic material will be taken into solution below pH 3 (Zereini et al. 1997). Lustig et al. (1997) showed that about 15% of Pt in tunnel dust from the ceiling of a road tunnel in Austria is extractable in the presence of EDTA. Previous investigations of soil processes have concentrated on Pt and Rh but some work on plant uptake by Schafer et al (1998) has indicated that Pd is more mobile than Pt or Rh.

The authors have been studying the roadside environment since 1993, when autocatalysts were first made compulsory on new cars sold in the UK. The first full study in the UK of the temporal variation of the PGE in road dust was carried out by the authors in 1995/96 (Piper, 1997), and then repeated in 1998/99 to evaluate temporal changes (Brown, 2002). In addition, a preliminary spatial study was carried out in 1995 at two sites of interest, with samples of surface soil taken at distances of 0-10 m from the road. This was followed in 1998/99 by a full temporal and spatial study of soil adjacent to the M40 motorway, UK, a study which was designed to examine the transport of the PGE in the environment. In this study samples were taken at depth as well as from the surface. The work presented here summarises the results of these studies with particular emphasis on the behaviour of Pd.

3.10.2 Methods

Sample collection

Road dust samples were collected at sites on two major roads on a weekly basis. Roads A (A30) and B (A355) are situated approximately 35 km south west of central London. Road A is a single carriageway major road with a traffic flow of 17,000 vehicles per day and has a speed restriction of 96 km/h. Road B is a dual carriageway with a mean traffic flow of 30,000 vehicles per day and a speed restriction of 64 km/h. Samples were collected on both roads between July 1995 and June 1996. This survey was repeated between September 1998 and August 1999. In November 1995 soil samples were collected adjacent to Road A at distances of 0, 1, 3, 5 and 10 m from both the north and south-bound carriageways, while at Road B soils were collected only on the east side. For further details, see Piper (1997). Surface soil samples were also collected 0, 1, 3, 5 and 10 m from the M40, a three-lane motorway with a speed limit of 112 km/h, between June 1998 and March 1999. In May 1998, soils were also collected at depths of 0-2 and 2-10 cm from this site.

The samples of road dust, typically weighing more than 10 g, were collected using a nylon brush and plastic collection pan. The collection area adjacent to the kerb was 1 m wide and ranged from 2 to 9 m long, depending on the quantity of dust available. Samples were dried at 50°C for 16 h and sieved to collect the fractions 63-250 μm and <63 μm. Soil samples were collected with a PTFE coated trowel. The surface soil was collected over an area of 0.5 m^2, to a depth of 0.02-0.04 m. Samples were dried at 50°C for 16 h and ground to a fine powder (<60 μm).

Sample preparation and analysis

The road dusts and soils were prepared using nickel sulphide fire assay, based on the method of Asif and Parry (1989). The advantages of this technique are that the PGE and Au are separated from the matrix and collected in a nickel sulphide button. A further benefit of the method is that relatively large, representative samples can be analysed. In addition, potential interferences during ICP-MS analysis from elements such as Hf and Pb are eliminated. Samples weighing 10 g are mixed with 10 g Na_2CO_3, 20 g $Na_2B_4O_7$, 2 g Ni powder and 1.4 g sulfur and heated to 1005°C in a fire clay crucible. After 2 h the mixture is poured into an iron mould and the NiS button separated from the slag on cooling. The button is crushed and dissolved in HCl. Tellerium and tin solutions are added to co-precipitate any PGE that have dissolved. The solution is filtered on cooling and the PGE dissolved in *aqua regia*. The solution is made up to 50 ml with deionised water ready for analysis by ICP-MS.

Instrumentation

Samples were analysed using a VG PlasmaQuad PQ2 ICP-MS instrument. The instrument was calibrated using matrix matched synthetic standards containing the PGEs at 0, 10, 20 and 50ng/g in 5%v/v aqua regia, and instrumental drift was monitored and corrected for using the 10ng/g standard. Elements were quantified using ^{195}Pt, ^{105}Pd and ^{103}Rh respectively. The NiS fire assay procedure separates the analytes of interest from the sample matrix and therefore potential interferences from species such as HfO and $^{206}Pb^{2+}$ are absent. Therefore no interference corrections were required.

3.10.3 Temporal variation

The first comprehensive UK study of PGE distribution in the roadside environment was carried out over a 12-month period in 1996/7. Road dust was collected weekly from two major roads. Roads A and B had mean traffic flows of 17,000 and 30,000 vehicles per day, respectively. An important aspect of the study was that all three PGE: Pt, Pd and Rh were determined simultaneously in the 63-250 μm fraction. The contrasting locations and seasonal collections provided the opportunity to study the effect of factors such as geographical location, topography, traffic flow and weather. An additional aspect of the work was that the 12-month study was repeated at the same sites two years later in 1998/9. This provided the opportunity to confirm trends identified in the initial work and to monitor changes as the number of vehicles fitted with an automobile catalyst increased and the different types of catalyst evolved.

The temporal study, carried out in 1995/6 provided a baseline of PGE concentrations showing that they varied throughout the year and almost doubled during the period monitored. The concentrations of PGE on Road A over the year were 10-100 ng/g Pt, 5 to 70 ng/g Pd and 1 to 20 ng/g Rh, while on Road B the concentrations were 100 to 600 ng/g Pt and 10 to 100 ng/g Pd and Rh. While elemental concentrations varied considerably throughout the year, the ratio of Pt/Rh was constant with a mean value of 6.6±1.7 and 8.5±1.0 on Roads A and B, respectively. The Pt/Pd ratios were 4.0±2.4 and 9.1±3.5, respectively. The larger ranges for the Pt/Pd ratios reflect the wider variation in the weekly Pd concentrations, compared to those for Pt and Rh. This was the first indication that the behaviour of Pd was different to that of the other PGE. The reason for the differences in the ratios of Pt/Pd and Pt/Rh between the two roads is not clear but Road B does carry more commercial (and hence diesel) vehicles and is close to a second input from a motorway passing close by.

When sampling was repeated in 1998/9, the concentrations of total PGEs had risen dramatically although traffic flows had remained essentially the same. For example, in samples taken from Road A the mean concentrations had increased by 232%, 1230% and 372% for Pt, Pd and Rh, respectively. The range for Pt had grown to 50-500 ng/g on Road A and 200-1,000 ng/g on the Road B. Pd had increased to 27-488 and 73-466 ng/g, respectively, and the values for Rh were 11-110 and 35-149 ng/g, respectively. We suggest that the largest increase, exhibited by Pd, was a direct result of the changing nature of the autocatalyst. The total concentrations of the PGE in

Table 3.10.1. Comparison of PGE in road dust

Location	Year	Size fraction	Mean Pt (ng/g)	Mean Pd (ng/g)	Mean Rh (ng/g)	Reference
SW Germany motorway	1997	Not given	59	-	10	Schafer et al (1999)
Gothenburg, Sweden (Urban)	1998	<63 µm & 63-250 µm	157 171	-	60 46	Rauch et al (2000)
Rome (Urban)	1998	<63 µm	41	243	6	Petrucci et al (2000)
Nottingham (Major/minor roads)	1998	<2mm	97	93	-	Hutchinson et al (2000)
Surrey/Berkshire (Major roads)	1998	<63 µm & 63-250 µm	298 204	187 126	53 37	This study (Brown, 2002)
Perth, Australia (Major roads)	2002	<63 µm	206	185	42	Whiteley and Murray (2003)

this study were typically higher than those determined in other European countries at the time, as shown in Table 3.10.1, but mean concentrations are in the same order of magnitude.

In the mid 1990s the use of Pd in autocatalysts increased dramatically and typical formulations included a Pt-Pd-Rh catalyst with Pt/Pd ratio of 0.6 and Pt/Rh of 2.5, a Pd/Rh catalyst with Pt/Pd of 0.6 and Pt/Rh of 5.2, and a Pt only catalyst for use on diesel vehicles (Palacios et al. 2000b). Therefore it was not unexpected that the ratios had changed between the 1996/7 and 1998/9 studies. The ratios of Pt/Rh had decreased on Roads A and B from 6.6 and 8.5 to 4.7 and 6.2, respectively, indicating a reduction of about 30% in Pt compared to Rh. The equivalent ratios for Pt/Pd were 1.4 and 2.1 in 1998/9, compared to values in 1995/6 of 4.0 and 8.2, respectively. These differences represent an increase in Pd of about 40%, assuming the reduction of 30% in the use of Pt.

3.10.4 Seasonal variation

The first study (1995/6) indicated a possible seasonal variation in PGE and this was confirmed in the 1988/9 study. This is seen most clearly in the plot

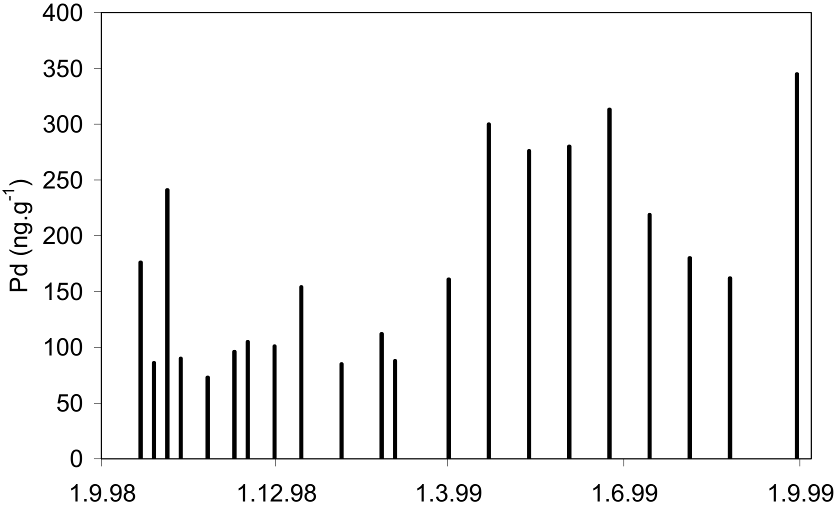

Fig. 3.10.1. Temporal variation of Pd on A355 (Road B) in 1998/9

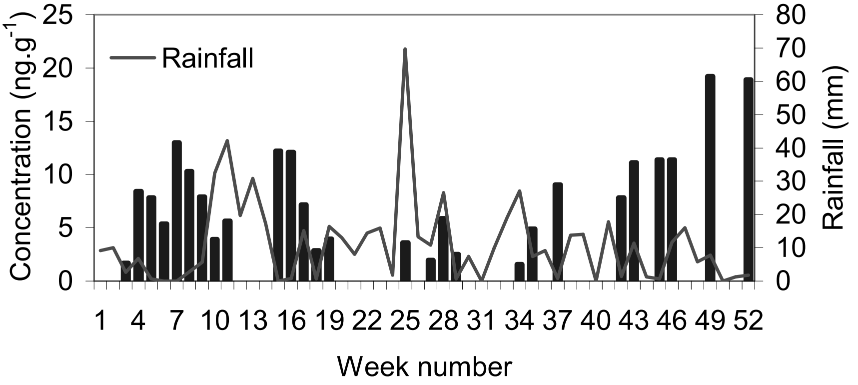

Fig. 3.10.2. Variation in Pd concentrations with rainfall on A30 (Road A) in 1995/6

of Pd concentrations on Road B from September 1998 to August 1999 in Fig. 3.10.1. The maximum concentrations for Pd occur in the summer months and the same behaviour is exhibited by Pt and Rh.

In 1995/6 there was evidence of lower concentrations of the PGE in periods of high rainfall as shown in Fig. 3.10.2. A similar study carried out in Australia (Whiteley, 2004) found that the lowest Pd values were also seen in road dust collected in winter. This coincided with the highest rainfall and

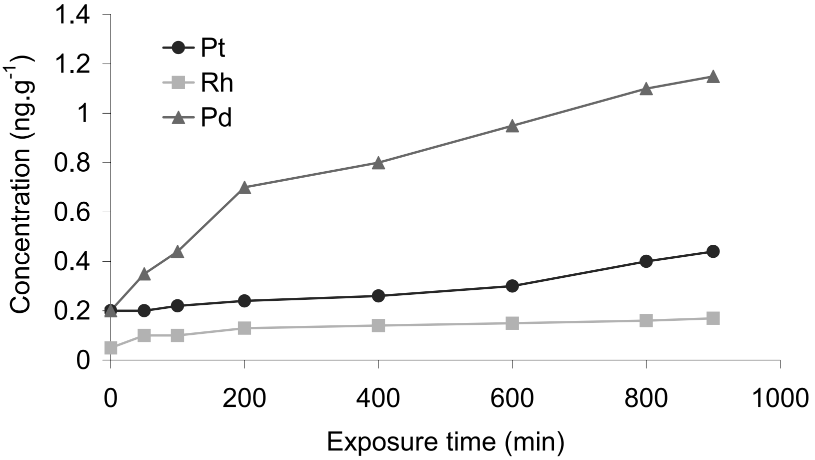

Fig. 3.10.3. Rate of solubility of PGE in road dust in simulate rain at pH 5.5

it is suggested by Whiteley that road runoff represents a major pathway for the mobilisation and removal of PGE. He also notes that the ratios of Pt/Pd are more variable than those of Pt/Rh but found no significant seasonal differences.

Weathering of metallic PGE is slow but can be facilitated by the presence of chlorides or possibly humic substances. The solubility of the PGE in road dust was tested by the authors using both deionised water and a simulated rainwater (Jarvis et al. 2001). When road dust containing 110 ng/g Pt, 3.4 ng/g Pd and 12.4 ng/g Rh was exposed to deionised water for 15 h, less than 1% of Pt and Rh dissolved but 6% Pd was solubilised. Simulate rain water at pH 3 had a similar effect on Pt and Rh but this time 35% of the Pd was dissolved in 15 h. Subsequently the experiment was repeated at pH 5.5 and the degree of solubility with time is given in Fig. 3.10.3.

The solubility rate for Pd is relatively rapid with 60% of the soluble fraction in solution after only 3.5 h. This would suggest that at least some of the Pd is present, not as a metal, but as a soluble species such as chloride. Artelt et al. (1999) have suggested that Pt is emitted from the exhaust in an insoluble form. If this is so and the chemical form of Pd is assumed to be similar, then the Pd speciation has changed whilst resident on the road surface. Since the sample of road dust used in the experiment had been on the road for less than one week, this transformation must be rapid. In addition, Palacios et al (2000a) have found the solubility of Pd and Rh to be higher than that of Pt in catalysts of various ages.

Table 3.10.2. PGE in road dust samples collected 1998/9

Road	Daily traffic flow	Size fraction	Pt (ng/g)		Pd (ng/g)		Rh (ng/g)	
			Range	Mean	Range	Mean	Range	Mean
A	17,000	<63 m	55 – 522	189	27 – 488	168	11 – 110	41
		63-250 m	36 – 336	106	23 – 301	97	9 - 74	22
B	30,000	< 63 m	188 – 1020	406	73 – 466	205	35 – 149	65
		63-250 m	122 – 799	301	54 – 269	155	21 – 111	52

Samples of road dust collected in 1998/9 were sieved to separate the 63-250 µm and <63 µm fractions, to investigate the distribution of the PGE particles. Table 3.10.2 shows that samples with the highest concentrations of the PGE are found in the fine (<63 µm) fraction. The behaviour of Pt, Pd and Rh is consistent, with the concentration of all three about 50% higher in the fine fraction, The ratios of Pt/Pd and Pt/Rh are constant in both fractions but they are different at the two sites. The Pt/Pd ratio is 1.1 at Road A and 2.0 at Road B while Pt/Rh ratios are 4.7 and 6.0, respectively

3.10.5 Spatial variation

Samples were collected along a transverse section on Road A on one occasion in November 1995. The concentrations of the PGE, shown in Fig. 3.10.4, varied by almost two orders of magnitude, from 0 to 10 m from the road edge. The sample taken at about 2 m on the east side displays a very low concentration and the control on this is not clear. Controls on the distribution are largely topographic, with a significant decrease in concentration for samples taken from a drainage ditch on the west side. This may be attributed to either removal in solution for more soluble species or by wash-out of particulate material. The ratios Pt/Pd and Pt/Rh are elevated at a point about 2 m to the east of the road, indicating that there may be preferential mobilisation of Pd and Rh at this point but the factor controlling that mobilisation is not clear. A rapid decrease in concentration, with a reduction of over 70% Pt from 0.2 to 1.2 m from the road, was also reported by Helmers (1996) from a German study of vegetation at the roadside.

In a more detailed soil study in May/June 1998 the authors investigated the distribution of the PGE between the upper horizon (top 2 cm) and the lower horizon (2-10 cm) at distances of 0-10 m on both sides of the M40

Table 3.10.3. PGE concentrations in soil adjacent to M40 motorway

PGE	Depth	Southbound						Northbound				
		10	5	3	1	0	Motor-way	0	1	3	5	10
Pt	0-2	1.2	3.2	6.7	21	22		60	20	3.9	2.0	2.2
	2-10	1.3	0.8	2.4	1.6	1.8		6.1	3.6	1.0	0.8	0.95
Pd	0-2	0.8	1.1	1.8	4.2	4.5		18	6.5	2.3	1.8	1.3
	2-10	1.1	1.0	1.6	2.3	2.9		2.9	2.2	2.4	1.2	1.2
Rh	0-2	0.3	0.6	1.0	2.8	2.9		9.6	2.9	0.7	0.5	0.4
	2-10	0.2	0.2	0.6	0.3	0.4		1.1	0.7	0.6	0.2	0.2

Motorway (Jaipal, pers. comm.). The concentrations of Pt, Pd and Rh are given in Table 3.10.3. Concentrations for all elements are higher in the top 2 cm of the soil profile and generally decrease rapidly within 1-2 m of the road. It would appear that Pd has been 'mobilised' from the upper 2 cm to

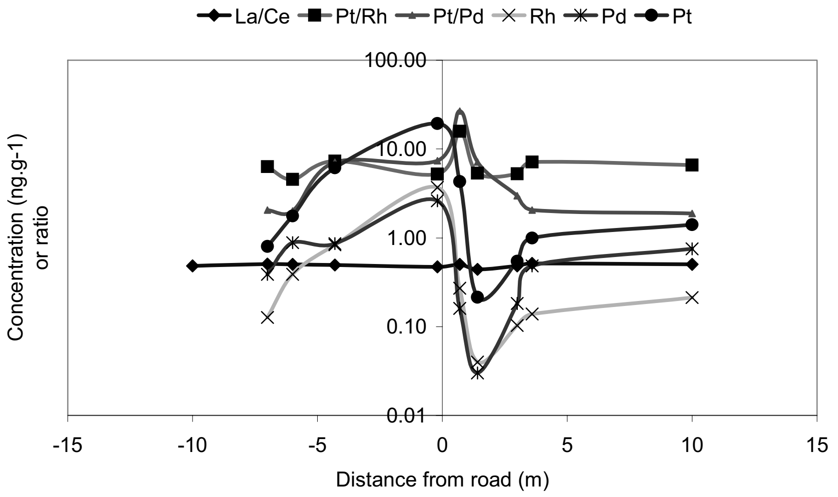

Fig. 3.10.4. PGE distribution patterns between 0 and 10 m to the west and east of Road A. The soil-derived La/Ce ratio is constant

deeper levels to a greater degree than either Rh or Pt. This is particularly apparent adjacent to the southbound carriageway. At 10 m there is no difference in the concentrations of the PGE between two horizons as background concentrations are approached. On the northbound side the concentrations are still slightly elevated at 10 m.

Previous work has suggested that PGE levels return to background within 10 cm depth (Schafer and Puchelt, 1998; Eckhardt et al, 2000; Zereini et al, 2000; Morton et al., 2001) but a detailed study of soil profiles in Australia (Whiteley, 2004) has shown that in sandy soil average levels of 10.6, 5.3 and 0.9 ng/g Pt, Pd and Rh are determined in cores taken 14-20 cm deep.

It has been proposed that differences in Pt/Pd in soil could be due to preferential mobilisation of Pd due to humic substances. The organic matter content at the surface was the same on both sides of the M40 motorway (8.5%) and not significantly different at depth (6.8% and 6.3% on the south and north sides, respectively); the pH was 7.2 on both sides. Therefore there was no obvious reason for the differences between Pt and Pd on the two sides of the motorway. However, it is possible that external influences, such as the use of road salt, could be important.

3.10.6 Characterisation of air particulates

The behaviour of the PGE in road dust would appear to be very different from that of particles emitted from the car exhaust. Work on atmospheric particles was carried out by the authors in the UK to characterise the nature

Table 3.10.4. PGE in PM_{10} in ambient air

Location & date	Pt (pg/m^3)		Pd (pg/m^3)		Rh (pg/m^3)		Reference
	Range	Mean	Range	Mean	Range	Mean	
Madrid (1997/8)	3.0-15.5	8.8			Nd-9.32	3.18	Gomez et al. (2000)
Rome (1998/9)	Nd-93.4	15.7	Nd-152	55.8	Nd-12.8	3.12	Petrucci et al. (2000)
London (2000)	Nd-121	33.9	11.9-93.3	33.4	Nd-23.2	11.1	This study Brown (2002)

Nd = not detected

Table 3.10.5. PGE in $PM_{2.5\text{-}10}$ and $PM_{2.5}$ in ambient air

Location & date	Particle size	Pt (pg/m^3)	Pd (pg/m^3)	Rh (pg/m^3)	Reference
Gothenburg (1999)	$PM_{2.5\text{-}10}$	14.1	4.9	2.9	Rauch et al (2000)
London (2000)	$PM_{2.5\text{-}10}$	32.6	30.6	10.4	This study Brown, (2002)
Gothenburg (1999)	$PM_{2.5}$	5.4	1.5	1.6	Rauch et al (2000)
London (2000)	$PM_{2.5}$	1.3	2.8	0.72	This study Brown, (2002)

of atmospheric particles of PGE. Samples of PM_{10} were collected at a busy roadside in London over a two week period in the summer of 2000. Maximum concentrations for the PGE in PM_{10} were 121 pg/m^3, 93 and 23 pg/m^3 for Pt, Pd and Rh, respectively. Mean concentrations were substantially lower at 34, 33 and 11 pg/m^3 , respectively. The results are higher but not dissimilar to those found by workers in other capital cities given in Table 3.10.4.

The work carried out by the authors showed that the PGE in ambient air are higher in the coarse fraction ($PM_{2.5\text{-}10}$) than in the fine fraction ($PM_{2.5}$). This type of work, characterising the two fractions, $PM_{2.5\text{-}10}$ and $PM_{2.5}$, has been carried out only once before, by Rauch et al. (2000). The sampling location in Gothenburg had a higher traffic flow (70,000 per day) than the London site (20,000) but the results were comparable, as shown in Table 3.10.5. Both studies demonstrate quite clearly that the PGE are concentrated in the $PM_{2.5\text{-}10}$ fraction.

3.10.7 Summary

In conclusion, the use of Pd in catalysts, in preference to Pt, has increased substantially since 1995 with significant consequences. The temporal studies show that Pd is more mobile in the roadside environment than either Rh or Pt, suggesting a transition from metallic form during residence on the road surface. Pd concentrations in soil profiles adjacent to the M40 motorway are consistent with this transformation either to chlorocomplexes, through reaction with salt, or with humic substances to form more soluble species. Comparison of the upper and lower soil horizons adjacent to the road indicates that Pd is mobilised and is transported further than Pt or Rh, If, as indicated, Pd is more soluble than Pt, it has the potential to contaminate water systems and agricultural land. Despite the increasingly large proportion of diesel cars being sold in Europe, representing 48% of all sales in 2003, the use of Pd will continue to have important environmental implications in the future.

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3.11 Spatial and Temporal Variation of Anthropogenic Palladium in the Environment

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3.11.1 Introduction

Palladium, one of the platinum group elements (PGEs), nowadays has received increasing attention in the production of automotive catalytic converters (ACCs) (Zereini and Alt, 2000). This is due to the exceptional catalytic properties of the metallic Pd amongst PGEs, which can be utilized to a rather efficient elimination of harmful and/or toxic components of exhaust gases (e.g., CO, NO_X, and hydrocarbons) released by diesel- and petrol-fuelled vehicles and some household utensils. However, the hot exhaust gases, which are conducted through the converters, cause the abrasion of the internal surface (activated with metallic PGEs) of these units, and results in the emission of PGEs into the environment. As it is known (Zereini and Alt, 2000; Ravindra et al., 2004), the levels of anthropogenically evolved PGEs have been continuously increasing in nature since the introduction of ACCs.

It appears that the risk of Pd to human health had been underestimated until the 80's. The allergic potential of Pd was first reported in connection with the use of Pd-rich dental restorative alloys (Van Ketel and Niebber, 1981; Castelain and Castelain, 1987; Aughtun et al., 1990). Similar observations were made with Pd chloride in human skin (epicutane) tests, which also revealed a distinct cross sensitivity to Ni. Around 90 % of the studied individuals, reacting against Ni, demonstrated sensitivity towards Pd (Olivarius and Menné, 1992). Occupational asthma caused by Pd metal has also been reported in one case (Daenen et al., 1999). In a recent study, Helm (2002) reported a likely association between elevated urinary Pd levels and diseases of the thyroid and the immune system. Therefore, it appears to be an important task to monitor the concentration of Pd in various environmental compartments and biological matrices to assess the risk of this element to human health.

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Table 3.11.1. Atmospheric concentration of Pd

City/Country	Other specification	Pd level ($pg\ m^{-3}$)	Reference
California, USA	freeway, 1974	<0.06	Johnson et al., 1976
Belgium, and Italy	-	<0.7	Schutyser et al., 1977
California	PM_{10}	1.0	Lu et al., 1994
Caesarea, Israel	$PM_{2.5}$ (1993)	3.3	Gertler, 1994
Chicago, USA	(1990)	12 700 (mean)	Scheff et al., 1997
Chernivtsi, Ukraine	(1990)	56 600 (mean)	
Czech Republic	various sites	30-280	Vlašánkova et al., 1999
Germany	background level	9-106	Rosner and Merget, 2000
Berlin	urban environment (1997)	0.2-14.6	Tilch et al., 2000
Rome	urban sites (1998-1999)	21.2-85.7	Petrucci et al., 2000
	urban site (1991)	<1.0	
Göteborg, Sweden	PM_{10} (urban area)	0.1-10	Rauch et al., 2001
Göteborg	1998-2000 (overall result)	4.1	Gómez et al., 2002
	downtown	4.6	
	ringroad	1.6	
	background	5.2	
Rome, Italy	1998-2000 (total result)	51.4	
	downtown	47.9	
	ring road	54.9	
	background	3.6	
Madrid, Spain	M-30 highway (PM_{10})	5.1	Gómez et al., 2003
	downtown	32	

(Part 1 of 2)

In the present study, an attempt is made to assess the spatial and temporal variation in the concentration of anthropogenic Pd in various environmental compartments, which can play a key role in the transportation, transformation and bioaccumulation of Pd, such as ambient air, roadside dust and soil, waters, river and oceanic sediments and vegetation.

Table 3.11.1. (cont.) Atmospheric concentration of Pd

City/Country	Other specification	Pd level (pg m^{-3})	Reference
Vienna, Austria	weekly range (average) PM_{10}	1.9-3.0 (2.6)	Kanitsar et al., 2003
	weekly range (average)	10.4-17.9 (14.4)	
	for particle size <30µm		
Vienna	2002 (downtown)	4-16	Limbeck et al., 2003
Salzburg, Austria	monthly average	7.1-31.2	Limbeck et al., 2004
Klagenfurt, Austria	monthly average	2.9-5.0	

(Part 2 of 2)

3.11.2 Level of Pd in airborne particulate matter

An overview on the Pd content of airborne particulate matter (APM) is listed in Table 3.11.1. The earliest monitoring results dating from the mid 70's were observed to be below 0.06 pg m^{-3} near a freeway in San Diego (Johnson et al., 1976) and lower than 0.7 pg m^{-3} in Belgium and Italy (Schutyser et al., 1977). These data are referred to as the background level of Pd in APM, as they had been obtained before the introduction of ACCs. Certainly, this approach neglects the impact of other possible anthropogenic emission sources of Pd, such as the dental alloy industry.

The Pd concentration significantly increased in APM in the 90's, due to the extensive usage of ACCs (Lu et al., 1994; Gertler, 1994; Petrucci et al., 2000). This increase was certainly proved to be higher in the U.S. than in Europe, due to the earlier introduction and usage of Pd-containing ACC units in the former area. From Table 3.11.1 it is also obvious that the diverse areas in Europe and America show a different pattern of their Pd content for outdoor aerosol samples. This is due to the rather varying nature of the sampling sites, e.g. diversity in the traffic intensity and morphologic/ geographical characteristic. At the end of 90's, generally, the level of Pd in APM samples were up to 300 pg m^{-3}, which is an increased value compared to the ones measured at the beginning of the 90's. This considerable raise in the anthropogenic Pd levels is due to the intensified usage of Pd in ACCs from the beginning of 90's.

Table 3.11.2. Pd concentrations in soil and road dust

Samples	Location	Other conditions	Level (ng g^{-1})	References
Garden soil	Nottingham, UK	1982	0.001-0.99	Hutchinson et al., 2000
		1996	0.02-1.11	
Roadside dust	Nottingham	1982	0.04-4.92	
	Residential streets	1996 (low traffic densities)	0.19-1.43	
	Major roads	1998 (high traffic densities)	5.6-556	
Roadside dust	San Diego (freeways)	1985, heavy traffic	38-280	Hodge and Stallard, 1986
	(residential streets)	1985, light traffic	15-24	
Continental crust			0.4	Wedepohl, 1995
Roadside dust	Germany	highway	1-146	Schäfer et al., 1996
Road dust	SW Germany	roads with heavy traffic	100	
Soil	Frankfurt-Köln track,	A3, Wiesbadener-Kreuz	6.6	Heinrich et al., 1996
Roadside dust	Frankfurt	1994	6-117	Zereini et al., 1997
Soil	Germany	-	1.2-12.5	Cubelic et al., 1997
Tunnel dust	Japan	1987	297	Helmers et al., 1998
Tunnel dust			20	
Roadside soil	Stuttgart, Heidelberg	highway	10 (max)	Schäfer and Puchelt, 1998
Road sediment			n.d.-28	Schäfer et al., 1999
Road dust	Sweden	-	56	Rauch et al., 1999

(Part 1 of 4)

According to Tilch et al. (2000), the weather and seasonal conditions did not have a noticeable influence on the PGE level, including Pd, in air. Although the use of Pd catalysts in 1997 was still limited compared to Pt- and Rh-based catalysts, the Pd content of air was found to be similar to that of Pt at the beginning of the 90’s.

Table 3.11.2. (cont.) Pd concentrations in soil and road dust

Samples	Location	Other conditions	Level (ng g^{-1})	References
Soil	Frankfurt	along motorways	6.0	Zereini and Alt, 2000
Soil	Frankfurt	in city area	4.0	
Tunnel dust	Theatre (Frankfurt)	1994 summer	40.3	Boch et al., 2002
	Harbor (Frankfurt)	1994 summer	113.7	
Tunnel dust	Candid (Munich)	Aug. 1994, (Febr. 2001)	13.5 (138.2)	
	Trappentreu	110 000 cars/day in 1994	17.7 (281.6)	
	Landshuter Allee	100 000 cars/day in 1994	21.8 (265.4)	
Tunnel dust	Candid (Munich)	94 000 cars/day (Aug 1997)	41.6	Schuster et al., 2000
	Trappentreu	126 000 cars/day (1998)	32.9	
	Landshuter Allee	118 000 cars/day (1998)	100.5	
Tunnel dust	Styria, Austria (Tanzenberg tunnel)	ventilation shaft, 1994, (1998)	4.0 (5.5)	Schramel et al., 2000
Road dust	Austria	highway tunnel	3.2	Müller and Heumann, 2000
Soil	Mainz, Germany	0.6 m	7.2	
		1.8 m	1.2	

(Part 2 of 4)

The sampling and analysis of size-segregated aerosols in Austria revealed that the PM_{10} fraction of APM (particles with an aerodynamic diameter below 10 μm) contained diverse amounts of Pd in Salzburg (monthly average: 7.1 to 31.2 pg m^{-3}) compared to Klagenfurt (2.9 to 5.0 pg m^{-3}). This was attributed to the diversity in the traffic intensity and the driving conditions between the two sampling sites (Limbeck et al., 2004).

Table 3.11.2. (cont.) Pd concentrations in soil and road dust

Samples	Location	Other conditions	Level (ng g^{-1})	References
		3.0 m from highway (BAB66)	1.1	
Soil	Darmstadt, Germany	near roads, highways	7.2-58.6	Patel et al., 2000
Road sediment	Göteborg, Sweden (1998)	<63µm particle fraction, and (63-250 µm particle fraction)	472 (395)	Rauch et al., 2000
Road sediment	Göteborg (1984)	<63 µm particle fraction, (63-125 µm particle fraction)	43.3 (54.1)	
Road dust	Rome, Italy	urban sites (heavy traffic)	102-504	Petrucci et al., 2000
Tunnel dust	Austria (Styria)	sampling from the ceiling	17.4	Köllensperger et al., 2000
Road dust		parking place (indoor)	108	Zereini et al., 2001
Tunnel dust			48	
Road dust	Göteborg, Sweden	1998, heavy traffic road (<63 µm particle fraction)	80	Motelica-Heino et al., 2001
Soil	Mexico City (Insurgentes/ Periférico)	(200 cars/min at rush hours)	53.2-74	Morton et al., 2001
	(Insurgentes/ Sta. Teresa)	low density (stop and go) (60 cars/ min at rush hours)	12.2-32.4	Morton et al., 2001
	(Periférico)	high traffic (constant speed) (110 cars/ min at rush hours)	15.2-82.7	

(Part 3 of 4)

With the use of Pd as an anthropogenic dilution tracer, it was possible to eliminate seasonal/meteorological variations and to determine changes in source emission or atmospheric transformation rates of PM_{10}-mass and elemental carbon concentration.

Table 3.11.2. (cont.) Pd concentrations in soil and road dust

Samples	Location	Other conditions	Level ($ng\ g^{-1}$)	References
	(Periférico/ Viaducto)	high traffic (constant speed) (180 cars min^{-1} at rush hours)	62.5-101.2	
Road dust	Madrid	ring road, city centre (<65 μm)	39-191	García et al., 2001
Road dust	Karlsruhe, Germany	road B10 (heavy traffic)	21.3	Sures et al., 2001
Urban soil			1.66	Dongarrá et al., 2002
Street dust	Germany	Saarbrücken	107	Kovacheva and Djingova, 2002
Road dust	Germany	motorway (A-1)	59	
		motorway (A-61)	95	
		highway (B-262)	68	
Road dust	Białystok, Poland	main crossroad (town)	36.6	Godlewska-Żyłkiewicz and Zaleska, 2002
Road dust	Warsaw, Poland		7.0	Chwastowska et al., 2004
Soil			8.0	
Soil	Napoli, Italy	suburban and urban areas	10-110	Cicchella et al., 2003
Road dust	Białystok, Poland	main road intersections in the city centre 30 000 vehicles/ day in 2000	32.8-42.2	Leśniewska et al., 2004
Tunnel dust	Białystok, Poland	(2000) <75 μm fraction	16.4-23.9	
		75-150 μm fraction	3.1	
Road dust	Saarbrücken	Ludwigskreisel	90	Djingova et al., 2003
		highway A1, A-61, B-262	95; 60; 82	

(Part 4 of 4)

3.11.3 Pd in soils, road-dust and vegetation

In soils, road-dust, and plants exposed to high-traffic density, the concentration of Pd far exceeds the natural background level (Tables 3.11.2 and 3.11.3). Hence, most of the studies have involved sampling of soil and veg-

Table 3.11.3. The level of Pd in plants

Samples	Location	Other parameters	Pd level (ng g^{-1})	References
Pine, birch, grass	Germany	80-120 000 cars/day (1995/96)	2.0	Helmers, 1997
Roadside grass	Munich, Germany	0.2 m from motorway	1.31	Schuster et al., 2000
		0.5 m from motorway	0.70	
		1.0 m from motorway	<0.3	
Grass	Warsaw, Poland		<0.2	Chwastowska et al., 2004
Pine needles	Palermo, Italy	Urban and rural areas (2000 June-July)	1-45	Dongarrá et al., 2002
Roadside grass	E67, Białystok	1 m, from highway (20 600 vehicles/ day)	3.2	Leśniewska et al., 2004
Pine needles	road E19, Poland	24 500 vehicle / day	n.d.	
Mushroom	Saarbrücken, Germany	Ludwigskreisel	0.2	Djingova et al., 2003
Moss			2.4	
Plantain			0.45	
Dandelion			0.83	
Plantain	Germany	highway A-1, road B-262	2.1; 0.5	
Dandelion		highway A-1, A-61, B-262	3.1; 1.5; 0.9	
Ryegrass		highway A-1, A-61	0.1; 0.1	

n.d. – not detected

etation adjacent to heavily traveled highways and of dust swept from the surface of roads. Analytical results of these types of samples have shown an upward trend of Pd concentration over time and a strong impact of the traffic conditions (Tables 3.11.2 and 3.11.3).

Hodge and Stallard (1986) observed extremely high levels of Pd, i.e. up to 0.3 ppm, in dust samples collected from the surface of leaves on roadside plants. The highest Pd levels were obtained in dust deposited on plants at the edges of streets and highways with heavy traffic, whereas the lowest concentrations were found in grass growing at the streets with light traffic. It was concluded that the dust accumulating along freeways and busy streets could concentrate upwards to 0.5 ppm Pd. These authors also deduced that the first rain after a long dry weather period, common in South California, would accumulate Pd containing dust from rooftops and streets in relatively large amounts of both soluble and insoluble forms, and transport them to the Pacific Ocean.

Ely et al. (2001) found a strong correlation of Pd with some traffic-related elements (Ni, Cu, Zn and Pb) in soils from US roadsides, but no correlation was found with other trace elements present in soils. In the heavily polluted Mexico City, the Pd contamination of soils exposed to high traffic densities exceeded the natural background values by up to two orders of magnitude and was also strongly dependent on the traffic conditions (Morton et al., 2001).

In Germany, nearby roads with heavy traffic density (100 000-120 000 vehicles per day), the Pt concentration in the 0.2 cm surface soil adjacent to the road ranged from several hundred ng g^{-1} to the local background value ($\leq$ 1 ng g^{-1}) at less than 20 m from the road (Schäfer and Puchelt, 1998). The PGE concentration significantly decreased in soil samples taken from deeper layers. Lateral and vertical distribution patterns for Pd were very similar to those observed by Eckhardt and Schäfer (1997). The Pd content of road dust ranged up to 100 ng g^{-1}, which is an indication of a short-term input of PGEs (Schäfer et al., 1996). Dust samples collected in the tunnel of 'Mittlerer Ring' in Munich, Germany, showed an increase in Pd concentrations from 21.8 ng g^{-1} in 1994 to 100 ng g^{-1} in 1997-98 (Schuster et al., 2000). This increase is much higher than the growth of the traffic density for the same period of time. It was also observed that the PGE contamination of the soil rapidly decreased with increasing distance from the highway.

Cubelic et al. (1997) found evidence for a significant correlation of PGE input and local conditions, such as traffic frequency, distance from the traffic-lane, prevailing wind direction, barriers, such as vegetation, and morphologic changes of the local environment. Schäfer and Puchelt (1998) observed that the distribution of PGEs in soils nearby roads is not only affected by the turbulence of vehicles passing along the roads, but the prevailing wind direction as well.

It has been shown that the short-term variation in the level of PGEs and their ratios in road dust were due to the wind and rain, whereas the long-term trends reflected the changing proportions of PGEs used for converter manufacturing (Schäfer et al., 1999). The integration of these data resulted in an estimate of the total PGE accumulation and the mean emission rates that were found to be significantly higher than those predicted from stationary car-engine experiments.

In a recent pilot study, Cicchella et al. (2003) analysed soil samples from downtown urbanized areas and suburbs of Napoli. The downtown soils showed a much higher Pd content than the suburban samples. The Pd found in downtown samples was identified as the emission product of ACCs. On the base of the high number of samples taken from diverse locations of the city, a geographic distribution map of the Pd pollution was established, which showed correlation of the level of this element with the road density and major traffic flows. The contaminated areas of the city have been found to be fairly large (13 km^2), which is supposed to be expanded in the future, implying the continuous increase of ACC equipped vehicles and the raise in the traffic density.

The occurrence of Pd in pine needles (*Pinus pinea* L.) collected in and around Palermo city, Italy were higher by two orders of magnitude than the crustal abundance, suggesting a common anthropogenic source, i.e., the ACCs (Dongarrá et al., 2002). The distribution of Pd in the pine needles was found to be highly non-homogeneous, which is a similar pattern as exists for APM.

From the data presented in Tables 3.11.2 and 3.11.3, in general, one can conclude that the concentration of Pd in road dust, soil and vegetation continuously increased for the last two and a half decades, and moreover, its levels do significantly depend on the local conditions of the monitoring site (i.e. vehicular density, wind direction, etc.). However, in several reports of the roadside vegetation, the data do not necessarily represent the real PGE uptake, rather the deposition, collection and adsorption of dust particles on the external surface of roadside plants (Rosner et al., 1991). This necessitates a standard sampling and sample handling procedure to be elaborated.

It is to be noted here that despite the results suggesting a drop in the Pd level of environmental matrices with increasing distance from the emission source, Van de Velde et al. (2000) observed an increased concentration of Pd (along with Rh) in ice and snow samples from Mont Blanc, especially, for the last decade. The fact that these Pd polluted places are located at high altitudes and far away from residential areas indicates a large-scale contamination impact of ACCs, likely via the transport of Pd as a component of APM through the troposphere of the Northern Hemisphere.

3.11.4 Pd in the water ecosystem

Several studies have given an account on the increasing concentration of Pd in various parts of the water ecosystem, i.e. rain, ground, and seawater; river and oceanic sediments, etc. (see Table 3.11.4). The enrichment of Pd in these matrices can mostly be linked to the release of this element from ACCs and it also supports evidence for post-depositional mobility of Pd in contaminated sediments.

Early studies on Pacific seawaters dating back to the 1980's reported very low levels of Pd, i.e. 0.04 ng l^{-1} (Lee, 1983). On the other hand, enhanced Pd levels were observed in freshly deposited coastal sediments in the moat that surrounds the Emperor's Palace in Tokyo. This local Pd gradient was attributed to the run-off from adjacent roads of frequent automobile traffic, as a consequence of Pd emission originating from the use of VECs.

The concentration of Pd in water from the Rhein and Schwarzbach rivers (Germany) was estimated to be at 0.4 ng l^{-1} (Eller et al., 1989), of which value is well below than those found in ground and rainwater. Hall and Pelchat (1993) determined Pd in fresh-water samples collected from some mineralized sites of Canada; dispersion patterns could be identified, but the maximum Pd concentration (dissolved fraction) was very low, i.e. below 5 ng l^{-1}.

De Vos et al. (2002) surveyed the distribution of all the PGEs in contemporary fluvial sediments of Kentish Stour (UK). The highest abundance occurred in motorway run-off sediments (maximum total PGE content of 55 ng g^{-1}, containing around 25 % Pd), whilst the lowest values were recorded in sedimentary rocks. The total PGE content of river sediments ranged from 0.4 to 10.8 ng g^{-1}. The authors concluded that the PGE distribution in sediments corresponded strongly with land-use changes (urban versus rural sections) and with the points of discharges from sewage treatment plants, but no clear single source signature could be identified, such as ACCs. This is probably due the contribution of other anthropogenic sources of the area studied (e.g. hospital effluents, and/or industrial activities) to the PGE content of river sediments, which, consequently, cause a shift in the concentration ratios.

The Pd concentration in the sediments of Boston Harbor increased around five times compared to the background levels detected in Massachusetts Bay, being referred to as an uncontaminated site (Tuit et al., 2000). Comparative analysis of the archived surface sediments from 1993 and 1996 revealed a 50-fold enhancement of the Pd concentration, compared to the level in 1978. This enhanced Pd level does not exceed that found in

Table 3.11.4. Pd levels in the water ecosystem

Samples	Location	Other parameters	Pd level (ng g^{-1}, if not indicated otherwise)	References
Seawater	Pacific Ocean	-	0.04 ng l^{-1}	Lee, 1983
River water	Germany	Rhein, Schwarzbach	0.4 ng l^{-1}	Eller et al., 1989
Fresh-water	Canada	mineralized sites	<5 ng l^{-1}	Hall and Pelchat, 1993
Rainwater	Germany		<5 ng l^{-1}	Helmers et al., 1998
Manganese nodules	deep-sea		3.7-11.4	Hodge et al., 1986
Sediment	Mölndal river	Göteborg, 1998	13.9	Rauch et al., 2000
Surface sediments	Boston Harbor	1987, 1993, 1996	19.93; 3.24; 4.22	Tuit et al., 2000
	Massachusetts Bay		0.6	
River sediment	Mölndal river	Sweden, 1999	38.7 (mean)	Moldovan et al., 2001
Sediment	Stour river	1999 June	0.08-5.71	De Vos et al., 2002
Snow	Greenland, the Alps	remote areas	0.00001-0.0169	Barbante et al., 1999, 2001
Ice, snow	Mont Blanc	remote areas	0.0005-0.01	Van de Velde et al., 2000
Urban river	Göteborg, Sweden	near a heavy traffic car park	10.2 ng l^{-1}	Moldovan et al., 2003

(Part 1 of 2)

deep-sea manganese nodules (Hodge et al., 1986). Although the concentration of anthropogenic Pd is relatively lower than found in other environmental matrices, a larger impact of this element can always be expected on aquatic life through bioaccumulation (Sures et al., 2001, 2002a; 2002b). It is to be noted here that anthropogenic PGEs, including Pd, have been found to be accumulated in some raptors (Jensen et al., 2002, Ek et al., 2004a),

Table 3.11.4. (cont.) Pd levels in the water ecosystem

Samples	Location	Other parameters	Pd level (ng g^{-1}, if not indicated otherwise)	References
European eels	Germany	exposed eel liver	0.14-0.25	Sures et al., 2001
		non-exposed eel liver	0.10	
Freshwater isopod (*Asellus aquaticus*)	Mölndal river, Göteborg	exposed	155 (dry weight)	Moldovan et al., 2001

(Part 2 of 2)

e.g., sparrowhawk (*Accipiter nisus*), and peregrine falcon (*Falco Peregrinus*). These studies have shown enhanced Pd levels in feathers, eggs, and blood from 1974 to 2000. It was also demonstrated that the enhanced PGE levels are due to an external exposure of these species, via inhalation of APM, or ingestion of their prey that was externally contaminated with PGEs (dust/APM).

The Pd contents of sewage sludge and effluent particles from Boston city were determined to estimate the magnitude of anthropogenic input. Boston sewage is a mixture of household and industrial waste, as well as road run-off, which is normally routed through the sewage treatment system of the city. The Pd levels found for the Boston sludge were similar to those reported for the sludge of New York, and additionally, to those reported for the sludge of 24 German cities (Lottermoser, 1994). The author implied that this enrichment is ubiquitous through industrialised areas. On the other hand, the higher Pd content of the sludge samples compared to Pt, suggested an additional anthropogenic source of Pd, and/or its more particle reactive behaviour than Pt.

Run-off increased the PGE content of urban sewage sludge, although its contribution was found to be less significant compared to other PGE emission sources (Schäfer et al., 1999). In a recent work, Helmers et al. (1998) explained the increased Pd content in the sludge of Stuttgart with an enhanced emission from the German dental-alloy industry. Other possibilities are the electroplating waste associated with jewellery and electrical industry, and most importantly, the chemical industry, which can release dissolved and/or readily dissolvable compounds of PGEs (Tuit et al., 2000).

3.11.5 Presence of Pd in biological matrices

Only few studies report the presence of Pd in human body fluids and tissues, because special attention has been given to Pt in comparison to the other PGEs. This is partly due to the extensive biomedical usage of Pt-containing anticancer agents, and partly to the prevailing presence of Pt in ACCs for the past two decades. Further, the analytical difficulties in measuring low concentrations of PGEs in biological materials have led to a lack of data on base-line levels, which makes health studies on human difficult. Recent studies demonstrated that Pd shows a grater tendency towards bioavailability (Sures et al., 2002a; 2002b; Jensen et al., 2002), and this makes assessing the possible effects of Pd on human health an important task.

Krächler et al. (1998) have proposed an ultra-trace method of analysis for PGEs and subsequently applied it to urine sample of 5-10 year-old school children from the urban and suburban areas of Rome. They found that the Pd concentration ranged from 5.2 to 14.8 ng l^{-1} with a median value of 9.5 ng l^{-1}. Caroli et al. (2001) also evaluated the exposure of 310 school children to PGEs in Rome. They have found an average level of 7.5 ng Pd per g creatinine, and observed a strong association of urinary PGE levels with traffic density in the area of residence. Begerow et al. (1997a) have also studied Pd in urine samples of 21 unexposed persons, whose Pd levels ranged between 33 and 220 ng l^{-1}. In another study on 9 unexposed persons, the Pd levels in urine ranged between <20 and 80 ng l^{-1} with a mean value of 39 ng l^{-1} (Begerow et al., 1997b).

Philippeit and Angerer (2001) have analysed urine samples of 44 persons (24 women, 20 men) from the general population, while 10 persons occupationally exposed to Pd were also analysed. The analytical results show that the Pd concentration ranged from <10 to 28 ng l^{-1} in general population, and from <10 to 2540 ng l^{-1} in occupationally exposed persons. Other studies conducted by Schuster et al. (2000) and Messerschmidt et al. (2000) have also shown relatively low concentrations of Pd in urine samples of the general population, i.e. <36 ng l^{-1} and <2.5 ng l^{-1}, respectively, whereas in the urine of occupationally exposed persons, the Pd concentration ranged between <80 and 3400 ng l^{-1} and between 200 and 1000 ng l^{-1}, respectively.

Begerow and Dunemann (2000) studied the exposure of the general population to Pd originating from the ACCs and dental restorative alloys. For volunteers with and without noble-metal containing dental alloys (Pd <0.05%), the urinary excretion of Pd ranged from 29 to 68 ng l^{-1} and from 27 to 82 ng l^{-1}, respectively. The urine samples of road workers, exposed to Pd emission by ACCs, have shown slightly increased Pd levels compared to school leavers (unexposed, control group).

Bocca et al. (2004) reported Pt, Pd and Rh concentration ranges in the urine of 257 subjects aged between 23 and 88 years. The subjects were selected from to Italian cities of diverse traffic densities, i.e. one with low traffic (Foligno) and one with high traffic (Rome). The concentration of Pd in urine samples ranged from 2 to 17 and from 0.7 to 17 ng l^{-1}, for Foligno and Rome, respectively, i.e. no significant difference has been found for this element. On the contrary, increased Pt and Rh levels were found in the urine samples of inhabitants in Rome compared to ones in Foligno.

These studies were conducted by applying an ultra-trace method for the determination of Pd with the aim of biomonitoring. There is not such study available that has been primarily focused on the exposure of biologic materials to Pd and its health effects. Further, these studies not only show a higher Pd concentration in biological matrices than Pt, but also significantly higher concentration in occupationally exposed persons, which likely indicates a higher mobility of Pd in biological materials, and hence demands to assess the effects of Pd in relation to human health.

3.11.6 Conclusions

The level of anthropogenic Pd, - mainly originating from the abrasion of ACCs, - shows a sharply increasing trend over time in various environmental compartments studied. However, the concentration of Pd differs in these matrices to a large extent. This is due to the rather changing conditions that exist in these environmental matrices, i.e., the distance of the emission source from the sampling site, the extent of dilution of Pd in the matrix, the morphologic characteristic of the site, the meteorological condition, etc. Moreover, the interaction of diverse environmental compartments with each other is also a condition, which has to be taken into account when evaluating the impact of Pd emission from ACCs.

In the latter context, the transport and transformation of Pd between diverse environmental compartments and its biological availability have been less investigated areas in this particular field of environmental science. Moreover, previous “speciation” studies are mainly focused on the characterisation of the molecular fractions of matrices to which Pt is bound, and only one study has so far been reported with respect to speciation of Pd (Weber et al., 2004). According to a comprehensive review on the environmental routes of PGEs to biological materials (Ek et al., 2004b), PGEs, and especially, Pd are transported to biological systems, which gives raise to the bioavailability of this element and its possible impact on health. Additionally, an important fact is the enhanced Pd levels in the urine of exposed and unexposed persons. Some other results on Pd analysis of urine analysis may suggest a less mobility and/or uptake of traffic related Pd compared to Pt and Rh. On the other hand, it can also be possible that the excretion of lower (non-occupational exposure) levels of Pd from human body takes place to a less extent compared to Pd and Rh, i.e the former element may be bioaccumulated in the human body. Therefore, it is to be supposed that studies on these interactions may receive an increased attention in the near future to understand the route of anthropogenic Pd in nature and to assess its risk to human health.

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3.12 Palladium in Environmental Matrices: A Review

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3.12.1 Introduction

Palladium is one of the Platinum Group Elements (PGEs) and it is present on the Earth Crust (EC) at very low concentrations. Background concentrations of these noble elements in the range 0.06-0.40 mg/kg were reported by Taylor (1985), Wedepohl (1995) and Rauch et al., (2000) while a Pd average concentration of 0.015 mg/kg in the Upper Continental Crust (UCC) was proposed by Greenwood and Earnshaw (1989) and Hartley (1991). In the last two decades the use of cars equipped with VECs (Vehicle Exhaust Catalyst) was strongly implemented in order to reduce the gaseous pollutants from vehicle exhausts. PGEs are present in catalyst owing to their chemical and physical properties. In fact, at the high operational temperatures of these systems (450-550° C), they facilitate the reactions that permit the transformation of about 90% of NOx, CO and HCs in the less dangerous products as N_2, water and CO_2. In modern three-way catalytic converters (TWCs), PGEs are dispersed in the honeycomb structure of the catalyst. However, notwithstanding the evident benefit, the continuous release of PGEs in the environment, following the deterioration of TWCs, produces some concerns. In fact in some urban areas the PGEs concentration in soils, sediments and dusts is slightly but continuously increasing, reaching in some cases values that are one or two order of magnitude higher than the natural background ones. In addition, the small particles of PGEs mainly are in the PM_{10} fraction where the < 3 µm breathable fraction could reach 35-40% of the emissions.

These concerns arise also considering recent data on PGEs demand for industrial use. In fact, since the introduction of catalytic converters a constant increase of these noble metals demand for application in auto catalysts has been observed. In Europe from 1992 to 2002 the total demand for Pt and Pd is grown of the 94.2% and 150% respectively, while their application for auto catalyst required the 75% and 84% of the total production. Worldwide data show that in the year 2000 rather 98% of the total mined Rh (16200 kg) has been used in car industry while the percentage for Pt and Pd was 31% and 61% respectively [WHO (1991, 2002), Johnson Matthey (2001), Ravindra et al., (2004)].

From when catalytic converters were first introduced, to comply with new legislation guidelines and thanks to technologic developments, catalysts have become increasingly efficient. Recently the importance of Pd has been hampered by the fact that the new three-way catalyst employ preferentially Pd and Rh instead of Pt which cost results too high for the market. So in the next future an increase on Pd emission can be reasonably expected and, cause to its highest mobility among PGEs a deeply investigation on Pd in environmental matrices should be promoted.

3.12.2 Palladium in Airborne Particulate Matter

Airborne Particulate Matter (APM) is characterized by very low levels of Pd which general range is <1-10 pg g^{-1} in extra urban sites, while in urban and heavy traffic areas the concentrations range from 10 to 300 pg g^{-1}. A paucity of data results for Pd in APM owing to detection limit of the proposed analytical procedures and for the presence of many interferences hampering the analysis of Pd at the very low concentrations. A further difficulty arises from differences in sampling methodologies and strategy (sampling time, sample volume, etc), that do not permit an immediate and easy data comparison. A data collection of Pd in airborne particulate matter is reported in Table 3.12.1.

Very high concentration values of Pd in APM have been found in Chernivtsi (Ukraine), where an ambient air study was done in 1990 following on ongoing occurrence of childhood illness evidenced that the pollutants involved were mainly present in airborne (Scheff *et al.* 1997). Analysis of total particulate matter evidenced elevated concentration of Pd (mean concentration of 56600 pg m^{-3}), with an enrichment factor of more than 200000. These data exceed also those measured in ambient air of heavy polluted cities as Chicago where a mean concentration of 12700 pg m^{-3} of Pd has been measured in 1990. Until today these results are the highest values reported in literature.

A range from 30 to 280 pg m^{-3} for Pd in APM for six different meteorological sites in Czech Republic has been reported by Vlašankova et al. (1999) in a methodological study where Pd was analysed with different methodologies by selective separation and preconcentration as Pd-chlorocomplexes.

Petrucci *et al.* 2000, in a study on PGEs concentration in APM in Rome, compare data of Pd levels from samples collected in different periods of the year in urban (high traffic) and remote (low traffic) sites. The study evidenced appreciable differences between urban (21.2-85.7 pg m^{-3}) and

Table 3.12.1. Palladium levels in Aiborne Particulate Matter (APM)

Location	pg m^{-3}	Remarks	References
California	1	PM $_{10}$	Lu et al. 1994
Caesarea (Israel)	3.3	$PM_{2,5}$ (1993)	Gertler 1994
Chicago (USA)	12700	1990	Scheff et al. 1997
Chernivtsi (Ucraine)	56600	1990	
Všechlapy (Czech Rep.)	30		Vlasankova et al. 1999
Sorolov	280		
Mdnec	31		
Rome (Italy)	4.6	Extra-urban site (1998)	Petrucci et al. 2000
	37.2	Urban site (September 1998)	
	63.3	Urban site (November 1998)	
	69.5	Urban site (January 1998)	
Germany	9-106		Rosner and Merget 2000
Berlin (Germany)	0.2-14.6	Urban area (1997)	Tilch et al. 2000
Göteborg (Sweden)	1.3-9.7	PM_{10} High traffic	Rauch et al. 2001
	<0.6-4.4	PM_{10} Low traffic	
	0.7-2.2	$PM_{2.5}$ High traffic	
	0.7-2.5	$PM_{2.5}$ Low traffic	
Madrid (Spain)	5.1-32	M-30 Higway	Gómez et al. 2003

(Part 1 of 2)

remote sites (4.6 pg m^{-3}), confirming the contribute of the release from catalytic converters to the environmental abundance of Pd. Discrepancies between PGEs ratios in the catalysts and in the samples have been found. Authors suggest that a possible cause could be an overestimation of the

Table 3.12.1. (cont.) Palladium levels in Aiborne Particulate Matter (APM)

Location	pg m^{-3}	Remarks	References
Vienna (Austria)	2.6	PM_{10} Weekly average	Kanitsar et al. 2003
	14.4	Weekly average < 30µm size	
Klagenfurt (Austria)	2.9-5.0	Monthly range 30000 car/day driving speed 20 km/h (2001)	Limbeck et al. 2004
	4.2	Cold season	
	3.5	Warm season	
Salzburg (Austria)	7.1-31.2	Monthly range 58000 car/day driving speed 70 km/h	

(Part 2 of 2)

analytes (overall for Pd), as a consequence of mass interferences. Otherwise a poor validity of commercial ratios of PGE in catalyst given by car maker cannot be excluded.

Pd determinations in 15 APM samples from Berlin were done by Tilch *et al.* (2000), applying the Graphite Furnace Atomic Absorption Spectrometry (GFAAS) and Laser Absorption Fluorescence Spectrometry (LAFS) methodologies. Pd levels in these samples ranged from 0.2 to 14.6 pg $m^{-3.}$. Any noticeable influence on these results can be related to meteorological and seasonal conditions. Pd concentration levels fall in the same range of Pt concentrations measured in 1991-92 by other authors. Comparable percentage of dust in the air were also calculated.

Data on Pd concentration in six PM_{10} samples of urban air from Göteborg have been discussed by Rauch *et al.* (2001). Samples derived from high traffic areas show the highest levels of Pd:1.3-9.7 pg m^{-3} for PM_{10} samples and 0.7-2.2 pg m^{-3} for $PM_{2.5}$ ones. In low traffic areas Pd levels are in the ranges <0.6-4.4 and 0.7-2.5 pg m^{-3} for PM_{10} and $PM_{2.5}$, respectively. Authors suggest that low traffic values can be considered as the "background" for urban atmospheric environment.

Gomez *et al.* (2003), in a methodological study on simultaneous determination by Te coprecipitation of PGEs in airborne and dust samples, deriving from selected sites along M30 highway and downtown in Madrid, found concentration levels of Pd in the range 5.1-32 pg m^{-3}. ^{105}Pd was the isotope selected for external calibration, while ^{106}Pd for isotopic dilution in order to avoid molecular interferences. The authors stress that this method is valid because the Te coprecipitation removes more than 95% of the interfering elements. However, there are some evidences that mathematical corrections are sometimes necessary.

PGEs size distribution is an important parameter to well understand the influence of the various sources that can give a contribution to urban aerosols. In fact, together with other parameters as composition, transport and residence time, could be used to understand the potential impact for human health. These aspects have been studied by Kanitsar *et al.* (2003), in a work mainly focused on the methodological aspects of PGEs analysis in size fractionated urban aerosols of Vienna. Pd and PGEs were found mainly in coarse aerosol fractions. The weekly average of Pd concentrations in <10μm fraction is 2.6±0.6 pg m^{-3}, while that of the fraction <30 μm is 14.4 ±3.1 pg m^{-3}. A similar size distribution is shown by all PGEs contained particle collective < 10 μm with a maximum in the 1-2.15 μm size. These authors evidence that this finding is important from a toxicological point of view because particle of these dimensions can easily and deeply penetrate in human lungs.

Data on Pd concentration in aerosol fraction <10 μm (PM_{10}) collected for one year study in two urban sites (Klagenfurt and Salzburg) in Austria, are discussed by Limbeck *et al.* (2004). Differences in Pd concentrations levels have been observed among the two cities while seasonal PM_{10} pattern are quite similar In Salzburg the monthly PM_{10} Pd concentration ranges from 7.1 to 31.2 pg m^{-3} while a lower range (2.9-5.0 pg m^{-3}) was found in Klagenfurt. These differences can be ascribed to high traffic intensity and different driving condition in Salzburg that can contribute to the high level of Pd in PM_{10}. In this study Pd is also considered as an atmospheric dilution tracer. With this approach it is possible to eliminate seasonal meteorological variability, to identify changes in source emission and differences in atmospheric PM_{10} transformation rates. Besides it is possible to calculate that ~20% of the enhanced PM_{10} mass in winter is mainly related to the reduced atmospheric dilution and not to meteorological changes.

3.12.3 Palladium in Exhaust Fumes

Direct determination of Pd and related PGEs in exhaust fumes permits to obtain information on their levels in car emissions. Difficulties arise in the sampling procedure, considering the differences in catalyst model and age,

Table 3.12.2. Pd emission rates in exhaust fumes

Catalyst type	Catalyst Components	Emission rate (ng km^{-1})	Remarks	References
Three-way	Pt, Rh	0.3*	Speed 140 km h^{-1}	Lüdke et al. 1996
Gasoline	Pt/Pd/Rh	1.2-1.9	Aged 18000 km, at 80 km h^{-1}	Moldovan et al. 1999
	Pt/Pd/Rh	2-24	Driving condition	
Gasoline	Pt/Pd/Rh	89-114	Fresh Catalyst	
Gasoline	Pd/Rh	18-23	Fresh Catalyst	
Diesel		3.6-6.2		
Gasoline	Pt/Pd/Rh	264±380§	Fresh Catalyst	Palacios et al. 2000
		12±5.7	Aged 30000 km	
Gasoline	Pt/Rh	246±378	Fresh Catalyst	
		15.9±5.1	Aged 30000 km	
Diesel	Pt	217±345	Fresh Catalyst	
		45.9±22.5	Aged 30000 km	
Diesel	Pt	27.1±49.4	Fresh Catalyst	
		81.5±75.3	Aged 30000 km	
Gasoline		14.2		Rauch et al. 2002
Diesel		75.8		

(Part 1 of 2)

speed and engine type, etc. Many authors have stressed that in real driving conditions car emissions result higher with respect to those measured under controlled condition in laboratory (Ravindra 2004; Cubelic 1997; Moldovan 2002). A collection of literature data is reported in Table 3.12.2.

Literature data are mainly focused on Pt and indicate, for this element, emission rate ranging from 7 to 123 ng m^{-3} corresponding to an emission factor of 9-124 ng km^{-1} (Artlet *et al.* 1999; Ravindra 2004). A tendency towards low Pd emission parallels the age of gasoline car catalyst. Recent direct determinations of PGEs in TWCs catalysts have evidenced that these

Table 3.12.2. (cont.) Pd emission rates in exhaust fumes

Catalyst type	Catalyst Components	Emission rate (ng km^{-1})	Remarks	References
Gasoline	Pt/Pd/Rh	22.0-108.0	Aged 0 km	Moldovan et.al. 2002
		1.4-19	Aged 30000-80000 km	
	Pd/Rh	15.5-132.1	Aged 0 km	
		1.9-21.5	Aged 300000-80000 km	
Diesel	Pt	4.2-84.4	Aged 0 km	
		4.0-110.4	Aged 30000-80000 km	

(Part 2 of 2)

* ng m^{-3}
Different catalytic converter from same manufacturer

elements are mainly present as metallic form in particulate. A percentage 85% has been calculate for Pd.

A concentration of 0.3 ng m^{-3} of Pd in car exhaust from a three-way gasoline engine car catalyst measured at the speed of 140 km/h had been found by Lüdke *et al.* (1996), applying the ETV-ICP-MS analytical technique. Samples fractions have been obtained with a multijet cascade impactor. The authors stress the importance to identify the relevant source for the particulate matter and to know and measure particulate size distribution, chemical composition, isotope ratio etc. The study of the distribution of PGE content per m^3 of exhaust fumes, in function of the aerodynamic diameter, evidence a good correlation between the couple Pt-Rh and Pd-Ir indicating that they are abraded from catalyst. Instead the poor correlation for Pt-Pd and Pt-Ir suggests different sources for Pd and Ir.

Moldovan *et al.* (1999), studying the release of PGEs from different type of catalysts, described a new sampling procedure to determine PGEs released in exhaust fumes from two different gasoline (Pt/Pd/Rh, Pd/Rh) and diesel (only Pt) car catalysts. The results obtained for aged catalysts (18000 km), were also discussed. Exhaust fumes were directly sampled from the end of the exhaust pipe by a newly developed sampling device.

The described procedure permits to collect the soluble and insoluble particulate fraction. Authors demonstrate that PGEs are mainly released as particulate form as a consequence of catalytic surface abrasion. In the particulate the metallic form of Pd is >85% while >90% results that of Pt and Rh. Pd amount emitted from fresh catalyst is higher with respect to that emitted from a 18000 km aged catalyst. Besides, the emission at constant speed (1.2-1.9 ng km^{-1}) is lower with respect those obtained with the simulated driving conditions that fall in the range 2-24 ng km^{-1}. Approaching this type of study it is important to know that a great variability in particles release occurs from catalyst of the same producer and also between samples from the same catalyst. In this work, evidence of Pd content in exhaust fumes from diesel catalyst are also reported. This evidence is in contrast with the composition of diesel catalyst where, as declared by manufactures, Pt is the unique PGE present.

The release of PGEs from different types of commercial TWC has been studied also by Palacios *et al.* (2000). The main task of this work was the study of the changes in the catalysts surface due to ageing of the catalyst. The research have monitored PGEs in exhaust fumes of new and medium aged car catalyst, collected directly from the exhaust pipe. It is possible to see that samples from fresh catalysts (0 km) show the highest PGEs particulate content, while after 30000 km an evident decrease of PGEs in gasoline and diesel catalyst emissions occurs. As an example, the mean of total Pd released from fresh gasoline catalyst is 250 ng km^{-1}. After 30000 km Pd emission decreases at 12-16 ng km^{-1}.

In a methodological paper, mainly focused on the on-line removal of Pd mass interferences in ICP/MS, Garcia *et al.* (2001) determined Pd concentration levels in the particulate fraction of exhaust fumes from TWC gasoline and diesel catalyst. Samples were collected simulating the extra urban drive cycle 91441 (EUCD) for light-duty vehicle testing, applying the same method previously described by Moldovan *et al.* (1999). Pd concentration in car exhaust fumes is comparable with those reported in other similar works.

3.12.4 Palladium in sediments

Relatively few data are available on Pd concentration levels on sediments. This is mainly related to the very low concentration of Pd in this matrix and, consequently, to the limitation produced by the interfering species at low concentration. However all studies evidence a clear increase of Pd and

PGE_S in the aquatic ecosystems reasonably related to the increase release of these elements from catalytic converters.

Data on Pd and Pt in oceanic sediments and Fe-Mn nodules have been given by Hodge et al. (1985), Table 3.12.3. This study evidences a marked Pt enrichment in oceanic water in comparison with Pd, suggesting that this element is more reactive than platinum in sea water. However, Pd is enriched in sediments owing to the scavenging reactions on inorganic and biological phases, while Pt is strongly enriched in Mn nodules than Pd if compared to their concentration ratio in sea water.

Pd concentration in river sediments have been determined by Rauch et al. (2000) in a methodological paper describing the performance of HR-ICP-MS instrument working at 10102 Δm/m, coupled with Ultrasonic Nebulizer. The influence of potential interferences were studied working both in High and Low resolution mode. The study of the interferences showed that Pd determination in sediments is strongly interfered by several molecular ion that can not be separated also with the HR mode.

Tuit et al. (2000) have analysed Pd and Pt in sediments from Boston Harbour to identify the contaminant sources and study the behaviour of these anthropogenic metals. This study evidences that the release of PGE_S from autocatalyst have produced an increased sediment inventories of Pd and Pt being the concentration range in deep Massachusetts Bay sediments 0.6±0.3 ng/g, significantly lower of the level reported in Table 3.12.8. These finding evidence that anthropic sources can influence Pd and Pt levels in coastal sediments and the widespread use of catalysts will cause enrichment in many urban coastal marine environments. This is supported by the finding that, reverse of others industrial metals, Pd and Pt inputs are not decreasing as displayed by the core profiles.

Moldovan et al. (2001) have studied Pd in the Mölndal river sediments (Goteborg, Sweden) evidencing that PGE_S accumulation is time dependent. The authors considered that PGE_S bioaccumulation in *Asellus Aquaticus* with the purpose to determine the relationship between exposures and bioaccumulation in a urban river collecting traffic pollutants. Two sites along the river were sampled. One located close to a parking area and the second near a highway with high traffic. Data are reported in Table 3.12.3.

Pd in river sediment of the Kentish Stour, England have been determined by De Vos et al. (2002) in a survey to document the sources and distribution of anthropogenic PGE_S. In these sediments Pd concentration level ranges from 0.08 to 5.71 ng/g. These levels are not consistent with the natural lithology that can influence the sources of the elements. In general Pd and PGE_S highest values correspond to urban areas heavy traffic and to the presence of discharge from sewage works. However authors stress that no clear

Table 3.12.3. Pd concentration levels in sediments

Location	ng g^{-1}	Remarks	References
Various oceanic basins	0.05-0.9	Deep sea, ferromanganese minerals	Hodge et al. 1985
1° N, 139° W	1.6	Carbonate ooze (depth 6-8 cm)	
	1.2	Carbonate ooze (depth 16-19 cm)	
11°N, 140° W	3.6	Siliceous ooze	
34°N, 120° W	0.8	Santa Barbara Basin (depth 10-11 cm)	
	0.7	(depth 13-14 cm)	
Göteborg , Sweden	14.9	Mölndal river (1988)	Rauch et al. 2000
Massachusetts Bay, USA	0.6±0.3	Deep sediment	Tuit et al. 2000
Boston Harbor	0.77-12.50	1978 Surface sea sediments	
	4.40-5.34	1993	
	3.72-4.42	1996	
Göteborg (Sweden)	43.7±3.5	1999 Mölndal river sediments, Site 1	Moldovan et al. 2001
	33.7±4.5	Site 2, river sediments	
Kent, England	0.08-5.71	1999 Stour river, sediment	De Vos et al. 2002

‘single-signature’, as those related to catalytic converters, were identified suggesting that the source characterised by signature could be variable or/ and mixed. Besides, a chemical fractionation for PGE_S as a consequence of changes in redox potential in fluvial environment can not be excluded.

3.12.5 Palladium in soils

Heinrich *et al.* (1996) reported data on Pd deposited in soils near Frankfurt, along A3 highway applying the INAA methods of analysis and the nickel sulphide fire assay as procedure to dissolve the sample. This analytical approach permits PGE determinations at very low (ng g^{-1} range) detection limits. These roadside soils evidence a strong Pd enrichment (6.6±0.19 ng kg^{-1}, Table 3.12.4) for samples close to the highway as evidenced from the concentration profile. In fact at 6 m from the highway Pd concentration level is six time lower while that of Rh is reduced by a 25 factor. Authors suggest that these findings could seen as an indication of a different mobility among PGEs in soil. However long term study are necessary to better understand mobilization and migration of PGE in soil.

To fill the gap on this research field, interesting considerations were done by Schäfer and Puchelt (1998) in an innovative work, mainly focused to study the distribution pattern of PGEs in some German soils in roadside environment. PGEs distribution is also compared with other traffic related elements as Pb and Zn. The effect of barriers in airborne transport and the influence of wind direction have been also considered. In fact, sampling sites were selected in relation to traffic density and site morphology. The results evidence that in top soil samples (0-5 cm) Pd concentration (< 0.3-10 ng g^{-1}) is higher than the natural background level. In roadside soils Pd level decreases significantly with depth and distance. As a consequence of the common source PGEs show a similar vertical and lateral pattern, while, with traffic related elements, differences occur in vertical distribution as a consequence of differences in particle size, mobility and soil residence time that is related to the recent introduction of PGE with respect that of Pb.

Müller and Heuman (2000), applying Isotope Diluition Inductively Coupled Plasma Quadrupole Mass Spectrometric method (ID-ICP-QMS), obtained simultaneous determinations of PGEs in soils. The concentration of Pd in top soil sample (0-5 cm), collected at different distances from the BAB 56 (highway near Mainz, Germany), ranges from 0.6-8.7 ng g^{-1} and an exponential decrease with distance from the highway has been observed for Pd and Pt. This evidence testify that PGEs are preferentially emitted from car exhausts as particles and not as gaseous components.

Determinations of Pd in three superficial soils samples collected close to an highway near Darmstadt, Germany, were given by Patel *et al.* (2000) in a methodological paper in which the technique of GF-AAS has been used. The method is based on a prior separation and enrichment of Pd as organic complex. The studied soils results contaminated in Pd being their concen-

Table 3.12.4. Pd concentration levels in soils

Location	ng g^{-1}	Remarks	References
Notthingham (U.K.)	0.64-0.99	1982 (42 samples)	Hutchinson et al. 2000
	0.21-1.11	1996	
Wiesbadener-Kreuz (Germany)	6.6±0.19	Highway A3	Heinrich et al. 1996
	1.2-12.5		Cubelic et al. 1997
Stuttgart, Heidelberg (Germany)	0.4	Highway, 100-120000 car/day	Schäfer & Puchelt, 1998
Various sites	<0.4-0.6	Quaternary sand and loess	
	0.6-1.2	Phonolitic rocks	
Frankfurt (Germany)	6	69 samples from motorway	Zereini et al. 2000
	4	City area	
Mainz (Germany)	7.2±1.5	0.6 m from highway	Müller & Heumann, 2000
	1.2±0.3	1.8 m from highway	
	1.1±0.5	3.0 m from highway	
Darmstadt (Germany)	7.2-58.6	Along highway	Patel et al. 2000

(Part 1 of 2)

trations in the range 7.2-58.6 ng g^{-1}. Authors stress that these results are lower than those found in San Diego urban soils (Cl., USA), that have a concentration of 300 ng g^{-1} of Pd.

Morton *et al.* (2001) have studied the concentrations of Pd and related PGEs in urban soils exposed at different traffic intensities in Mexico city (Table 3.12.3). In this city one third of the 4 million circulating cars have a catalytic equipment. Samples were collected at different depths and distances from traffic line with the aim to obtain information on PGEs mobility. Two "pre-anthropic" soil samples were analysed to obtain Pd background concentrations. In Mexico city soils have higher Pd levels that are 20-30 time that of background. Urban areas with constant traffic speed

Table 3.12.4. (cont.) Pd concentration levels in soils

Location	ng g^{-1}	Remarks	References
Mexico City (Mexico)	2.5-8.3	Pre-anthropogenic	Morton et al. 2001
	69.9	90 cars min^{-1} at rush hour	
	46.8-74	200 cars min^{-1} at rush hour	
	12.2-32.4	60 cars min^{-1} lower traffic	
	15.2-82.7	110 cars min^{-1} high traffic, constant speed	
	62.5-101.2	180 cars min^{-1} at rush hour	
South Bend (In., USA)	2-31	Roadside soil	Ely et. al. 2001
Perth (Austalia)	8.8-14.4	Roadside soil	
Palermo (Italy)	1.66	Urban area (information value)	Dongarrá et al. 2003
Naples (Italy)	< 10-110	195 soil samples from low-high traffic areas. Parent materials: pyroclastic rocks	Cicchella et al. 2003
	0.6-1.2	Phonolitic rocks	

(Part 2 of 2)

have Pd and PGEs lower levels with respect those with “stop and go” traffic. Pd level decreases with distance from roads and with sampling depth. In fact, at the depth of 7-10 cm has been measured a concentration of 7.2 ng g^{-1} of Pd that is close at the background level. Authors stress that, although Pd and PGEs are present in these soils in relative low concentrations their increase in the last years is evident and that the introduction of car catalysts will change dramatically their distribution in the urban environment in the next decades.

A detailed study to assess the Pd and PGE content in top soils and grasses from South Bend, Indiana, (U.S.A) has been done by Ely *et al.* (2001). Authors stress the importance to establish PGE background levels to determine the exact anthropic contribution. Considering that PGEs levels in soils are related to geological and mineralogical composition of local bedrock, for data normalization can be used local natural soil with a composition similar to that of roadside soils. Pd abundances along highway and several urban sites range from 2-31 ng g^{-1}. These levels are statistically above local soil background. A positive correlations between PGE and traffic-related elements (Ni, Cu, Zn, and Pb) has been also found. For comparison authors report data on roadside soils from Perth, Australia (Table 3.12.4) not showing the same degree of enrichment in PGEs as South Bend road soils. Instead these value are comparable to those of some European urban soils where, sometimes, concentrations reach levels that could even be considered economically viable to recover. The study also evidence that automobile catalytic emissions contribute to soil pollution along motorway and that at 50 m from the road Pd concentration is still above the background levels. As general consideration authors evidence that the differences in Pd and PGEs concentration observed in roadside soils all around the world, indicate a lack of information concerning PGE behaviour in roadside environment. More geochemical information on mobility, bioavailability, and toxicity to be combined with other extremely variable factors as climate, traffic intensity, age and type of catalyst, etc., are necessary to better understand the fate of these pollutant in soil.

In Italy data on Pd in urban soils are reported by Cicchella *et al.* (2003) that have studied Pd and Pt distribution in 195 top soil samples from the metropolitan area of Naples. In these soils, derived from the same parent material (pyroclastic rocks of the Flegreian Fields), Pd levels ranges from <10-110 ng g^{-1} with a mean of 12.7 ng g^{-1}. A strong correlation between Pd content and heavy traffic roads arises from study of geochemical maps, suggesting that these levels are related to vehicle exhausts emissions. Cumulative frequency plot for Pd show the existence of three different populations. The first with low values 8-18 ng g^{-1}, another with high Pd levels > 71 ng g^{-1} and a ‘mixed’ population that encloses samples in the range 18-71 ng g^{-1}. Sample from low population could be considered representative of the local background in relation to the parent materials, while high level population is related to anthropic contamination.

3.12.6 Pd in dust

A collection of data on Pd in dust sample is reported in Table 3.12.5. Dust is a very complex matrix, composed by heterogeneous material that can be characterized by very high PGEs content. Until now researches have been mainly focused on Pt and Rh determinations owing to the analytical problem related to the very low levels of Pd in dust and to the high level of the analytical interferences (^{105}Pd was the isotope preferentially selected for the final MS detector determination, because it is not subject to isobaric interferences).

Hodge and Stallard (1986) have reported data on Pd concentrations in dust collected from the leaves of Agapanthus and Hedera plants species growing along roadside in San Diego, California. An evident difference in Pd content in dusts was found between samples from low and heavy traffic conditions. In fact the level of Pd in dust collected from plants close to roads with intense traffic reached 0.28 μg g^{-1}, while dust from plants of residential streets have a Pd concentration of 0.015 μg g^{-1}. The ratio Pt/Pd was 2.5 in agreement with the ratio found in catalysts at that time. Authors stress that the release of Pd and other PGEs from cars may not only impact the environment close to roads, but also waters and sediments. In fact, owing to the effect of runoff, soluble and insoluble forms of Pd can be easily accumulated and then transported, overall after the relatively long period of dry weather that are common in California.

Müller and Heuman (2000), report a concentration of 3.2±0.4 ng g^{-1} of Pd in a road dust sample collected on a filter system of a highway tunnel in Austria. The research is part of an interlaboratory study among 15 laboratories of the European Union organized by the BCR (Standards Measurement and Testing Program), for the determination of PGEs using different analytical methodologies. At the same project it is referred the work of Schramel *et al.* (2000) that describes the main analytical and methodological aspect of this trial. For Pd a very large data scattering has been observed and was explained by the effect of cadmium and yttrium oxide interferences. Matrix separation is suggested even if HR-ICP-MS is employed.

Pd determination by HR ICP-MS in road dust samples from different sites of Rome has been reported by Petrucci et al (2000). Differences in Pd levels in road dust samples from suburban (low traffic) and urban (high traffic) areas were observed being the mean level 11.8±0.7 and 243±156 ng g^{-1}, respectively (range 102-504 ng g^{-1}). The wide concentration range 11-504 ng g^{-1} of Pd in road dust is the evidence of poor homogeneity of this material. A spot comparison between these data with those of samples collected in 1991 confirm the increase of PGEs as a contribute from catalytic converters. The same consideration arises from the work of Cinti *et al.* (2000) on Pt distribution in urban and natural soils of Rome and the surrounding region.

Schuster *et al.* (2000) have studied dust samples collected in the tunnel of 'Mittlerer Ring 'in Munich, Germany. A collection of these data are reported in Table 3.12.4. This research evidences an increase in Pd concentrations from 21.8±3.5 ng g^{-1} in samples collected in 1994 to 100.5±15.1 ng g^{-1} in dust sampled from 1997 to 1998. This Pd accumulation in tunnel dust results much higher respect to the growth of the traffic density for the same period of time and stress the peculiarity of the conditions that influence dust accumulation (continuous cycles of suspension and deposition) in a particular environment as tunnel is.

A level of 17.4±2.3 ng g^{-1} of Pd in road dust samples from the ceiling of a tunnel in Styria (Austria) have been measured by Köllensperger *et al.* (2000). This work is mainly focused on the methodology of the direct ICP-SFMS (Sector Field Mass Spectrometry) determinations of PGEs in road dust. The authors, with the aim to mitigate spectral interferences, have combined the high mass resolution capability and ultrasonic nebulization combined with membrane desolvation. Dust samples were collected in 1995 and the Pt/Pd was found to be 3.7 evidencing the enrichment of Pd in fine fraction of the tunnel dust as reported by others studies. This is also the consequence of the relatively high reactivity and mobility in aquatic media of Pd with respect others PGEs.

Applying the laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS), Motelica-Heino *et al.* (2001) determined Pd levels in road sediments from Göteborg, Sweden (Table 3.12.4). These samples were collected close to a heavy traffic road in 1998 and these data were compared with similar road samples collected in 1984 considered relatively free from PGEs presence. Because the aim of the work was to asses the suitability of LA-ICP-MS technique, Pd determinations were performed, for comparison, with the HR-ICP-MS methodology. The average of Pd in road sediment determined with LA-ICP-MS was 80±13 ng g^{-1}, while the concentration determined in HR-ICP-MS is slightly lower 68±5 ng g^{-1} This discrepancy evidence that Pd determination is influenced by interferences that can not be reduced or eliminated even working in high resolution mode.

On a temporal study over 12 months on PGEs distribution along adjacent two major U.K. roads, Jarvis *et al.* (2001) have found elevated levels of these elements in road dust, all above those of the background. For Pd the highest concentration was 70 ng g^{-1}. Authors evidence that Pd and PGE levels show a high variability throughout the year and seem to be slightly correlated with rainfall. Among PGEs Pd manifests the highest solubility (up to 30% of the total Pd is soluble in acid solution), evidencing an high dissolution rate and mobility. Authors point out that this finding could have significant consequences for Pd transport in aquatic environment where chloride species prevails on the metallic form. This could also produce some concerns considering the increasing Pd demand for catalyst of new generation.

Pd concentration levels in roads dust samples from different sites along some German highways have been reported by Kovacheva and Djingova (2002), in a methodological study which have used the ion-exchange procedure with Dowex 1-X10 resin and thiourea as an eluating agent. In these road dust samples Pd levels range from 56-114 ng g^{-1} and a good agreement has been found between ICP-AES and ICP-MS determinations of the same sample.

In a work that describes the development of a microwave-assisted digestion procedure to determine Pd in road dust, Boch *et al.* (2002) report data from several tunnel dust samples collected in Germany in the period 1994-2001. Respect to other urban dust sources, tunnel environment result less influenced from atmospheric effects. This fact permit to observe that, in Munich, from 1994 to 2001 Pd increases from 13.5±3.7 ng g^{-1} to 138.2±13 ng g^{-1}, a level that is considerably high with respect to the increase of traffic in the same period.

Data on Pd in some environmental matrices have been reported by Leniewska *et al.* (2004a, Table 3.12.5) in the framework of a pilot study in Bialystok, northeast Poland. The study was also performed to compare Pd determinations with TXRF (Total Reflection X-ray Fluorescence) and HR-ICP-MS techniques. Pd levels obtained with TXRF result lower while no significant differences in results are produced by HR-ICP-MS and Q-ICP-MS, confirming that ICP-MS technique is the more reliable method for Pd and PGE determination in environmental matrices. In road dust samples the mean concentration for Pd is 32.8 ng g^{-1} if TRFX method is applied and 42.2 ng g^{-1} by HR-ICP-MS. Pd enrichment has been observed in the < 75μm fraction of road and tunnel dusts.

Data on Pd concentration levels in dust collected in the main and heavy traffic tunnels of Rome, produced in the E.N.E.A. (Italian National Agency For Energy And The Environment) laboratory in which are working the authors of this chapter, have been reported in Table 3.12.5. To reduce the great heterogeneity of the dust (tunnel can be considered a very complex ‘environment’ characterized by scarce homogeneity and with a high variability for the particles composition and depositional modality), a composite sample was obtained mixing three samples collected inside an area of about one square meter. Very high levels of Pd result from this study. The highest Pd concentration was found in samples from Muro Torto Tunnel (832 ng g^{-1}) that, among these tunnels is the longest and the heaviest trafficated.

Table 3.12.5. Pd concentration levels in urban dust

Location	ng g^{-1}	Remarks	References
San Diego (USA)	38-280	Dust from surfaces leaves of Agapanthus and Hedera sp. Major freeways > 96000 car/day (1985)	Hodge & Stallard 1986
	15-150	Residential streets Agapanthus, Hedera and Pyoporum sp. <14000 car/day	
Germany	1-146	Higway	Schäfer et al. 1996
Frankfurt	6-117		Zereini et al. 1997
Japan	297		Helmers et al. 1998
Sweden	56	Motorway	Rauch et al. 1999
Germany	n.d.-27.2	Urban area	Schäfer et al. 1999
Nottingham (U.K.)	0.69-4.92	1982 (n=10 samples)	Hutchinson et al. 2000
	0.19-1.43	1996 (n=8)	
	5.6-556	1998 (n=20)	
Styria (Austria)	3.2±0.4	Highway tunnel, (1998) <90µm fraction Interlaboratory study	Müller & Heumann 2000
Styria, (Austria)	4.0±1.3	Ventilation shaft, Interlaboratory study	Schramel et al. 2000
Rome (Italy)	102-504	Heavy traffic	Petrucci et al. 2000
Munich (Germany)	41.6±12.2	940000 car/day (Candid)	Schuster et al. 2000
	32.9±10.1	126000 car/day, Trappentreu (1998)	
	100.5±15.1	118000 car/day, Landshuter Allee	

(Part 1 of 3)

Table 3.12.5. (cont.) Pd concentration levels in urban dust

Location	ng g^{-1}	Remarks	References
Austria	5.5	Ventilation shaft, (1998)	
Styria, (Austria)	17.4±2.3	Tunnel ceiling	Köellensperger et al. 2000
Göteborg (Sweden)	80±13	Heavy traffic	Motelica-Heino et al. 2001
England (U.K)	1-70	Road A355, 32000 car/ day;	Jarvis et al. 2001
Madrid (Spain)	39-191	City center	Garcia et al., 2001
Saarbrücken (Germany)	56-114		Kovaceva & Djingova. 2002
	95±2	Motorway A1	
	82±7	Motorway A61	
	60±4	Higway B-262	
Karlsruhe (Germany)	21.3	Road B10 Heavy traffic	Sures et al. 2001
Munich (Germany)	13.5±3.7 41.6±12.2 138.2±13.0	1994 Candid tunnel 1997 2001	Boch et al. 2002
	17.7±4.1 32.9±10.1 281.6±28.8	1994 Trappentreu tunnel 1998 2001	
	21.8±3.5 100.5±15.1 265.4±9.9	1994 Landshuter Allee 1998 2001	
Frankfurt am Main (Germany)	40.3±12	1994 Theatre tunnel	
	113.7±35.4	1994 Harbor tunnel	
Bialystok (Poland)	42.2±1.0	Road dust, (<75µm fraction)	Leniewska et al. 2004a
	23.9±1.2	Tunnel dust, (<75µm fraction)	
	3.10±0.41	(75-150µm fraction)	

(Part 2 of 3)

Table 3.12.5. (cont.) Pd concentration levels in urban dust

Location	ng g^{-1}	Remarks	References
Rome (Italy, 2004)	271±16	Castel S. Angelo Tunnel (opened from 2000)	Angelone et al. 2004 (this study)
	307±23	Fleming Tunnel (renewed in 2002)	
	567±157	Principe Amedeo Tunnel	
	832±4	Muro Torto Tunnel (the oldest tunnel in Rome)	

(Part 3 of 3)

This level of concentration has been already found in another situation by Schäfer *et al.* (1999) studying PGEs in road dust in Germany. Pd concentration levels in tunnel dust of Rome results to be related to the tunnel age. As an example, Castel S. Angelo tunnel has been opened to traffic circulation only in 2000 and Collina Fleming tunnel has been recently renewed: samples from these sites have a Pd concentration of 271±16 and 307±23 ng g^{-1}, respectively.

3.12.7 Palladium in snow and water

Palladium determination in water is difficult cause to the very low Pd content and the matrix interferences. For these reasons, few studies have been exploited with a particular regard to the improvement of analytical techniques. A data collection is reported in Table 3.12.6.

Barbante *et al.* (1999) studied snow and ice samples coming from Greenland, Antarctica and the Alps and covering different time periods. In a longer time scale, comparing the PGE concentration of very old Greenland ice dating back seven millennia (Holocene) with the values of recent samples, it can be seen that the concentration of these elements are several times higher than the background natural Holocene levels (0.01 pg g^{-1}). In the snow samples dated from 1969 to 1975, just before the introduction of automobile catalytic converters, Pd concentration was already 15-fold the natural level and its value increased 80 times during the two decades 1976-1995. In this work it has been also studied seasonal variation of Pd and other heavy metals in central Greenland snow deposited from 1991 and 1995 (see also Barbante et al., 2003).

Table 3.12.6. Pd in Snow and waters

Location	Concentration	Remarks	References
		Water	
Pacific Ocean	40 pgl^{-1}		Lee 1983
Germany	0.4 ngl^{-1}	Rhein river	Eller et al. 1989
Göteborg (Sweden)	10.2 ± 1.0ngl^{-1}	River	Moldovan et al. 2003
		Snow and Ice	
Alps, Greenland Antarctica	0.01-16.9 pg g^{-1}	Snow and ice in remote areas	Barbante et al. 1999; 2001
Central Greenland	0.05-2.7 pg g^{-1}	Seasonal variation in snow	Barbante et al. 2003
Mont Blanc	0.5-10 pg g^{-1}	Remote areas	Van de Velde et al. 2000
Kola Peninsula, Russia	<1-2770 ng l^{-1}	Snow collected from localities close to the nickel processing centers	Gregurek et al. 1999
Chamonix Valley, French Alps	1.6-4.2 pg g^{-1}	Fresh snow collected at various altitudes	Veysseyre et al. 2001
Maurienne Valley, French Alps	2.3-4.2 pg g^{-1}		

Gregurek *et al.* (1999) collected snow samples in the vicinity of the nickel processing plants on Kola Peninsula. Particulate material on snow was analysed and it appeared evident that concentrations of PGEs increase with proximity to the industrial sources. The prevailing wind direction also play an important role in the distribution. Concentration level up to 2770 ng L^{-1} of Pd was found near a smelter complex.

Veysseyre *et al.* (2001) measured heavy metals concentration in fresh snow collected at different altitudes in the Chamonix and Maurienne valleys, French Alps. Pd concentration shows rather constant trend irrespective of the altitude of the sampling site and enrichment factor values (vs. Al) over 10000. Authors suggest that this metal probably originates from long-range transport from distant anthropic sources.

Moldovan *et al.* (2003), utilised on-line preconcentration of Pd on Alumina microcolumns for the analysis of urban water samples like urban river and fountains water. The urban river water was collected in Göteborg (Sweden) in a sampling site close to a parking area with high traffic density while fountains waters were collected in Madrid (Spain) from three different fountains located in high traffic density area and platinum concentration was also determined. In each fountain Pd content is higher than Pt one, in contrast with the composition of the automobile catalyst where Pt is the major constituent. This fact could be interpreted as an evidence of the higher mobility and solubility of Pd with respect to the Pt.

3.12.8 Palladium in biological materials

In recent years, the increased use of PGE and Pd, in particular, has led to several investigations on possible biological accumulation of platinum group elements. Few studies were exploited on natural levels of exposed or unexposed materials, while many articles are devoted to bioaccumulation studies under laboratory conditions. A recent review summarises the literature on environmental routes for PGE to biological materials (Ek et al., 2004a). In general, it has been demonstrated that PGE emitted from automobile catalysts can be transformed into soluble species in soil or water by complexation with organic matter; Pd shows, among PGE, the highest solubility and toxicity.

Animals

Exposure studies were carried out on PGE bioavailability for aquatic animals, in this field there is an urgent need for validated analytical procedures with high detection capacities for the determination of Pd due to its low concentration in biological materials, but, till now, no biological standard reference material is certified for PGE. A data collection is reported in Table 3.12.7.

In general it was demonstrated that organisms maintained in water containing road dust were able to accumulate Pd (Sures et al., 2001, 2002). In particular, for zebra mussels the degree of bioavailability increased in the following manner: Rh<Pt<Pd. Moldovan et al (2001) investigated the ability of *Asellus aquaticus* to accumulate PGEs under natural and laboratory

Table 3.12.7. Pd in animals

Location	ng g^{-1}	Remarks	References
Mölndal river, Göteborg (Sweden)	155.4±73.4	*Asellus acquaticus* (Isopod)	Moldovan et al. 2001
Lake Mondsee (Austria)	3.25	Exposed *Dreissena polymorpha* (zebra mussels)	Sures et al. 2002
Germany	<0.10	Unexposed eel liver	Sures et al. 2001
	0.18	Exposed eel liver	
Sweden	0.6-2.1	Feathers from different bird species	Jensen et al. 2002
Sweden	0.8	Blood of *Falco Peregrinus*	Ek et al. 2004 a,b
	0.5	Eggs	
	0.7	Liver	
	0.3	Kidney	

exposure conditions. The exposure to PGEs standard solutions for a period of 24h give bioaccumulation factors of: 150, 85, and 7 for Pd, Pt and Rh, respectively. The bioaccumulation is time dependent and shows a higher accumulation for the materials with a higher PGE content: car catalyst powder.

Instead natural PGE concentrations were determined in birds that are useful bioindicators for temporal and spatial exposure. In Sweden, Jensen et al. (2002) collected and analysed feathers of sparrowhawk, peregrine falcon, gyrfalcon, willow grouse and house sparrow. The raptors studied have different food choice, habitat and migration patterns. Mean concentration of Pd after 1986 ranged from 0.6 to 2.1 ng g^{-1} (indicative value). No significant spatial trend could be established probably cause to the widespread distribution of automobiles and to the bird migration.

Ek et al. (2004b) measured PGEs in eggs of the sparrowhawk and the peregrine falcon and in blood, liver and kidney of the peregrine falcon. These birds are found in both rural and urban environments and migrate and forage over large areas. By comparison of data from 1974 to 1977, no significant temporal trend could be established. Higher relative concentrations of Pd, followed by Rh and Pt, indicate a mobility gradient of Pd>>Rh>Pt.

Table 3.12.8. Pd concentration levels in Plants

Location	Plant	ng g^{-1}	Remarks	References
Germany	Pine, birch, grass	2		Helmers 1998
Munich (Germany)	Roadside grass	1.31	0.2m from motorway	Schuster et al. 2000
		0.70	0.5m from motorway	
		0.5	1.0m from motorway	
USA	Roadside grass	0.97-1.44		Ely et al. 2001
Poland	*Poa trivialis* (grass)	3.2±0.23	Roadside grass collected in 2000	Lesniewska et al 2004a
Germany	*Taraxacum officinale*	0.68-3.5	Four sampling sites	Djingova et al. 2003
	Plantago lanceolata	0.27-2.3	Three sampling sites	
	Lolium multiflorum	0.07 - 0.13	Two sampling sites	
	Vascellum pratense	0.2 ± 0.1	Mushrooms	
	Rhytidiadelphus squarrosus	2.4 ± 0.3	Moss	
U.K.	Sycamore, beech, poplar and horse chestnut	1.6-3.2	Tree bark from rural areas, cities and industrial areas	Becker et al. 2000
Palermo (Italy)	Pinus pinea	1-45	Pine needles in urban and rural areas	Dongarrá et al. 2003

Plants

The occurrence of palladium in plants is related to the presence of PGE_S in airborne particulate matter emitted from catalytic converters and then deposited on soil and plant leaves. Plant analysis is very useful to monitor the PGEs emission during a defined short period of time or during the whole vegetation period. An exposure of a few months is long enough to observe and measure the metal emission within one year.

A comparison between data is not easy cause to the different experimental conditions of each study: plant species, plant parts (leaves, roots or shoots), sampling sites (traffic intensity and distance from the street), weather conditions before and during sampling, type of soil (this factor might influence bioaccumulation mechanisms). Furthermore Palladium determination in plants is difficult cause to the very low Pd content and the matrix interferences.

Dongarrà *et al.* (2003), Table 3.12.8, investigated Pd content in pine needles that can be used as practical indicator in PGEs monitoring due to the long life and low cost of sampling, besides this tree is widely spread in the study area and it was already been used for biomonitoring heavy metals distribution in the same area. Samples were collected in Palermo (Sicily, Italy), in the city center and in the surroundings. Observed concentrations range from 1 to 45 ng g^{-1}, the highest values occurring in the sites with heavy traffic.

Djingova *et al.* (2003) collected different plants along German highways and street in 1999 with the aim to evaluate $PGEs_S$ and other traffic-related elements distribution among plants used for this purpose as heavy metals biomonitors. The selected species were dandelium (*Taraxacm officinalis*), moss (*Rhytidiadelphus squarrosus*), mushrooms (*Vascellus pratense*) and annual ryegrass (*Lolium multiflorum*).

Many works were realized on bioaccumulation studies, but in general these experiments were carried out under unnatural conditions: hydroponic cultures, greenhouse experiments with temperature and humidity different from outdoors, soils with high doses of well-soluble PGEs salts. All these factors increase the transfer and therefore the obtained results could be unrealistic, however PGEs bioaccumulation should be studied to better understand their metabolism pattern and the probability that these metals enter in the food chain and can cause a direct effect on human health. Lesniewska *et al.* (2004 b), for example, studied bioaccumulation of PGEs by grass grown hydroponically with nutrient solutions enriched with Pt, Pd and Rh. The highest bioaccumulation factors were obtained for Pd and Rh in roots and for Pt in leaves, the results show that each metal has a different metabolism pathway, but only small amounts of metals were really metabolised and transported to the leaves with a minimum risk to enter in the food chain.

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4 Bioavailability and Biomonitoring of Palladium

Studies of various environmental media clearly show autocatalysts are a primary source of the widespread distribution of PGE. Their bioavailability or potential to be taken up by plants and animals is, thus, an important issue. This chapter contains five different sections which discuss issues and present data related to the bioavailability and biomonitoring of Pd.

Zimmerman & Sures in Section 4.2 discuss the bioavailability of Pd to terrestrial and aquatic animals. In Section, Thielen et al. investigate the use of different plants and fauna as accumulation indicators to monitor Pd in the environment. Ayrault et al. (Section 4.4) examine the feasibility of using moss to assess Pt and Pd pollution in the region of Paris, France. The topic of PGE bioavailability and bioaccumulation is also discussed by Ek et al. in Section 4.5 in the context of research conducted on the distribution of these metals in free-living birds of prey. Sures et al. (Section 4.1) provide an overview of the biological effects of Pd, with a focus on the genotoxic, allergenic and carcinogenic potential of this metal and its toxicity at the cellular and organism level.

Not much is known regarding the behaviour of Pd in the environment, particularly its bioavailability and bioaccumulation potential in plants, animals and humans. Experimental work shows that soluble forms of Pd are taken up in greater amounts by plants and aquatic animals compared to Pt. Palladium appears to be the most biologically available metal of the PGE (Section 4.2, 4.3). Although present levels of Pd in the environment are relatively low, the demonstrated bioavailability of this metal indicates that there is a need to monitor it in the future.

Zereini & Alt (Editors)

4.1 Biological Effects of Palladium

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4.1.1 Introduction

The still increasing use of platinum group metals (PGM) has resulted in a widespread introduction and distribution of these metals in the environment. The uptake and accumulation of Pt, Pd and Rh has been demonstrated for various organisms including humans. Among the PGM Pd has a very high biological availability as shown for plants and animals (summarized in Hoppstock & Sures, 2004; Zimmermann & Sures, 2004). Consequently, it is important to understand the biological and toxicological effects of Pd as compared with Pt and Rh but also in comparison with other metals such as Pb, Cd, etc. A comprehensive summary on the toxicity and environmental health criteria for Pd is presented by the World Health Organization (IPCS 2002).

4.1.2 Genotoxicity of Pd

Due to the use of certain Pt compounds and their effectiveness in cancer therapy, different Pd based substances have also been tested in respect of their genotoxicity. For chemotherapeutic purposes Pt compounds with the structure *cis*-PtN_2X_2 are commonly used as they are strong mutagens (Uno & Morita 1993), whereas the mutagenicity of *trans*-platin is considerably lower (Beck & Fisch 1980). DNA replication and mitosis are inhibited by the formation of DNA adducts of Pt(II) complexes. The mechanism of the genotoxicity of cisplatin (*cis*-diamminedichloroplatinum) was summarized in Gebel (2000). Due to high extracellular concentrations of chloride (100 mM), Cl^- binds to the cisplatin molecules, which pass the cellular membrane by diffusion. In the cytoplasma two chloride ligands diffuse away from cisplatin because of the low intracellular Cl^- concentration (3 mM), which results in the formation of electrophilic *cis*-$Pt(NH_3)_2^{2+}$ forms. These ions are able to bind to the DNA, resulting in interstrand adducts, intrastrand adducts and DNA-protein crosslinks (Pinto & Lippard 1985).

A great number of Pd compounds tested - among them divalent *cis*-complexes – failed to show any evidence for a genotoxic potential to bacterial systems. The Pd compounds $PdCl_2$, K_2PdCl_4, *cis*-$Pd(NH_3)_2I_2$, *cis*-$Pd(NH_3)_4Cl_2$, and the corresponding *trans*-Pd compounds did also not show any genotoxicity in human lymphocytes. As the atomic radius of Pd is smaller than that of Pt, a divalent *cis*-complex of Pd will quickly decompose to Pd^{2+} and the respective ligands in solution. This might be the reason why none of the Pd compounds tested so far was mutagenic in contrast to the effects of *cis*-platinum compounds. A couple of mutagenicity tests with bacterial or mammalian cells using different Pd compounds failed to show a mutagenicity (details in IPCS 2002). Also micronucleus tests in the mouse did not produce positive results (Johnson Matthey, 1998). In general, Pt and Rh compounds show stronger genotoxcicity (likely mediated by oxidative damage induction of DNA) than Pd salts do (Migliore et al. 2002).

However, genotoxic effects of Pd particles with a size of approximately 0.25 to 0.5 µm have been recently investigated using mammalian cell cultures (Hartwig et al. 2002). These experiments demonstrated a dose-dependent induction of DNA adducts after exposure of alveolar epithelial cells (A 549) towards Pd particles. This was the first proof that PGM particles can be taken up by phagocytosis, enter the nucleus and bind to DNA. Following these preliminary studies, further experiments are necessary to estimate the genotoxic potential of particulate PGM including Pd. Such studies are appreciated as 11 to 36 % of the particles emitted from automotive catalytic converters show a size of < 3.14 µm (Artelt et al. 1999). Particles ≤ 10 µm reach the tracheobronchial region with a likelihood of $\geq 50\%$, whereas particles ≤ 4 µm are mainly respirable, i.e. deposit in the alveolar region of the human lung (DFG 1997). Therefore, this fraction of particles may represent a toxicological risk for humans.

4.1.3 Carcinogenicity of Pd

There is only limited information available on the carcinogenic potential of palladium. One study was published that indicates a carcinogenicity of $PdCl_2$ administered during lifetime (from weaning to natural death) to mice (Schroeder & Mitchener 1971). There was a significant increase in the occurrence of malignant tumors compared with a simultaneous control group. However, interpretation of the data is difficult as the increased tumor rate might be caused by a significantly prolonged longevity of the exposed animals. Furthermore, no information on the dose-response relationship was available and the tumor rates were not differentiated between the sexes of the animals.

4.1.4 Allergological potential of Pd

Effects of Pd have been reported mainly due to iatrogenic exposure. Pd sensitivity occurs associated with exposure to Pd containing dental restorations (see overview in IPCS 2002). Symptoms such as contact dermatitis, stomatitis or mucositis and oral lichen planus have been described. However patients with positive $PdCl_2$ patch test did not necessarily react to metallic Pd. Side effects from other medical or experimental uses of Pd preparations include fever, haemolysis, discoloration or necrosis at injection sites after subcutaneous injections and erythrema and oedema following topical application (IPCS 2002). Compared with other allergens, Pd belongs to the seven most frequently reacting sensitizers (ranked second after nickel within metals). However, solitary Pd reactions occurred with a low frequency, whereas mostly combined reactions with other metals, primarily nickel, have been observed.

4.1.5 Cellular toxicity of Pd

There are numerous *in vitro* studies on the cytotoxicity of $PdCl_2$ and $PdSO_4$ (see overview in IPCS 2002). Inhibition of DNA synthesis (Nordlind 1986, Wataha et al. 1991a & 1995a, Nordlind & Liden 1993, Schedle et al. 1995) and RNA synthesis (Mital et al. 1992) have been shown. Protein synthesis was also inhibited or a decrease in total protein content or mitochondrial activity was found (Clothier et al. 1988, Wataha et al. 1991a & 1995a, Schmalz et al. 1997). Several other cell functions were severely affected by exposure to Pd^{2+}. However, the effects depend on the test systems und parameters used. The effects on DNA-, RNA- and protein synthesis as well as the decrease in mitochondrial activity occurred generally at lower Pd concentrations than those that caused cell lysis (Wataha et al. 1995b). LC_{50} (concentration resulting in 50% mortality) determined with mouse, hamster and human cell lines by analysing the mitochondrial dehydrogenase activity (MTT assay) ranged between 134 to 360 µmol/L Pd (Wataha et al. 1991b & 1995b, Schmalz et al. 1997). Recent studies using the human alveolar cell line BEAS-2B exposed to different metals revealed a LC_{50} of 400 µmol/L (MTT assay) for $PdSO_4$ which was the same as determined for $Pt(NO_3)_2$ (Sures & Zimmermann 2004). Among the metals tested, the highest toxicity was determined for $CdCl_2$ with a LC_{50} of 5 µmol/L, followed by CrO_3 with a value of 20 µmol/L. In comparison, the toxicity of $RhCl_3$ and $NiCl_2$ were considerably lower with LC_{50} of 1200 µmol/L and 800 µmol/L, respectively (Sures & Zimmermann 2004).

As a main conclusion it emerged that Pd ions are capable of inhibiting a number of cellular functions. Concerning the MTT assay Pd shows a relatively high toxicological potential compared with other metals.

4.1.6 Organismic toxicity of Pd

Several Pd compounds have been found to elicit antiviral, antibacterial and/or antifungal effects (see IPCS 2002). Additionally, micro toxicity tests were performed by CEPLACA (2001) to determine EC_{50} (concentration producing a certain effect in 50% of the test organisms) for soluble chloride compounds of Pt, Pd and Rh with *Photobacterium phosphoreum*. After 30 min of exposure the EC_{50} was 130 µg L^{-1} for Pt, 90 µg L^{-1} for Pd and 96 µg L^{-1} for Rh. This toxicity was much higher than for other metals commonly occurring in road runoff like Pb and Cu. Accordingly, adverse effects of Pd compounds (and other PGM) in the environment on micro organisms cannot be excluded. However, data obtained under environmentally realistic conditions are not available at the moment.

Concerning toxicity tests with higher organisms, very few information are available for terrestrial species. However, a basic data set exists on the acute toxicity of different Pd compounds to mice, rats and rabbits (summarized in IPCS 2002). LD_{50} (dosis resulting in 50% mortality) values ranged between 3 mg/kg body weight ($PdCl_2$, intravenous, rat) to >4900 mg/kg body weight (PdO, oral, rat). As a general conclusion from the studies using mammals as test organisms it appears that oral administration caused the lowest toxicity due to the poor uptake rates.

Most of the limited data available on the toxicity of Pd for higher organism was obtained in studies with aquatic organisms. After exposure of the water hyacinth (*Eichhornia crassiceps*) to potassium tetrachloropalladate (II) and chloropalladosamine chlorosis, necrosis and stunted dark roots were detected (Farago & Parsons, 1985 & 1994). Using necrosis as a measure of toxicity the following order was found among the PGM tested: Pt(II), Pd(II) > Ru(III), Ru(II), Ir(III) > Pt(IV), Os(IV) >> Rh(III).

Acute toxicity data were evaluated for different Pd compounds using different aquatic animals such as the crustacean *Daphnia magna* (Johnson Matthey 1997a) and the fish species medaka (*Oryzias latipes*) (Doudoroff & Katz 1953) and rainbow trout (*Oncorhynchus mykiss*) (Johnsson Matthey 1997b). Interestingly, the comparison between Pt and Pd revealed that Pd ($PdCl_2$) was twice as toxic as Pt (H_2PtCl_6) when applied to medaka (LC_{50} for Pd: 40 µmol/L, LC_{50} for Pt: 80 µmol/L) (Doudoroff & Katz 1953).

In addition to studies addressing the acute toxicity of Pd to aquatic animals, other experiments have investigated sublethal effects. Using the freshwater tubificid worm *Tubifex tubifex*, 96-h EC_{50} values have been determined for 31 metals (Khangarot 1991). Pd was found to have an EC_{50} value of 92 µg/L which was the sixth toxic element among the metals tested after Os, Ag, Pb, Hg and Pt.

A series of studies has also been conducted using the zebra mussel *Dreissena polymorpha* as a test organism. This mussel is widely accepted in ecotoxicological research and is commonly used for monitoring water contamination (Sures et al. 1999, Roditi et al. 2000). Furthermore *D. polymorpha* turned out to be very efficient in accumulating PGM (Zimmermann et al. 2002, 2005, Singer et al. submitted a). During a 10 weeks exposure study using soluble salts of Pd, Pt, Rh, Cd and Pb, mussels were sampled weekly, to determine the uptake and accumulation of metals and to correlate metal levels with biological effects. As representative effect-biomarkers the levels of heat shock proteins with the molecular weight of 70 kDa (hsp70) and of metallothioneins (MT) were analyzed in the soft tissues of *D. polymorpha* (Singer et al. submitted a & b). Heat shock proteins are widespread in plants, bacteria and animals and belong to the chaperones, which are very important for protein folding, protein transport and cell stabilization (Schröder et al 1999, Werner & Hinton 1999). In terms of ecotoxicological research these proteins are important biomarkers for a wide range of stressors including metal pollution, and their induction is accordingly a sign for adverse effects of the substances tested (Sanders 1993). Metallothioneins are metal binding and detoxifying proteins with a low molecular weigth (6-7 kDa), which are rich in cystein (Kägi & Schäffer 1988, Nordberg 1997). They are inducible in almost all organisms by exposure to different metals such as Cd, Ag, Hg and others. However, there is no information on the induction of MT due to Pd exposure until now, although it is reported that Pt can induce MT synthesis in rabbits (Zhong et al. 1997). If PGM induce MT, this can be interpreted as a clear sign of the necessity to detoxify these metals. Furthermore, MT might then be used as relatively specific biomarkers as not all metals tested so far are able to induce MT synthesis (Park et al. 2001).

Comparing metal concentrations in mussel tissue during the 10 weeks exposure, highest metal uptake was found for Cd, followed by Pt, Pb, Pd and Rh (Singer et al. submitted a). This metal accumulation was also associated with a significant increase of hsp70 levels in all groups of mussels compared with the control (see Fig. 4.1.1 for Pd and Pb as examples).

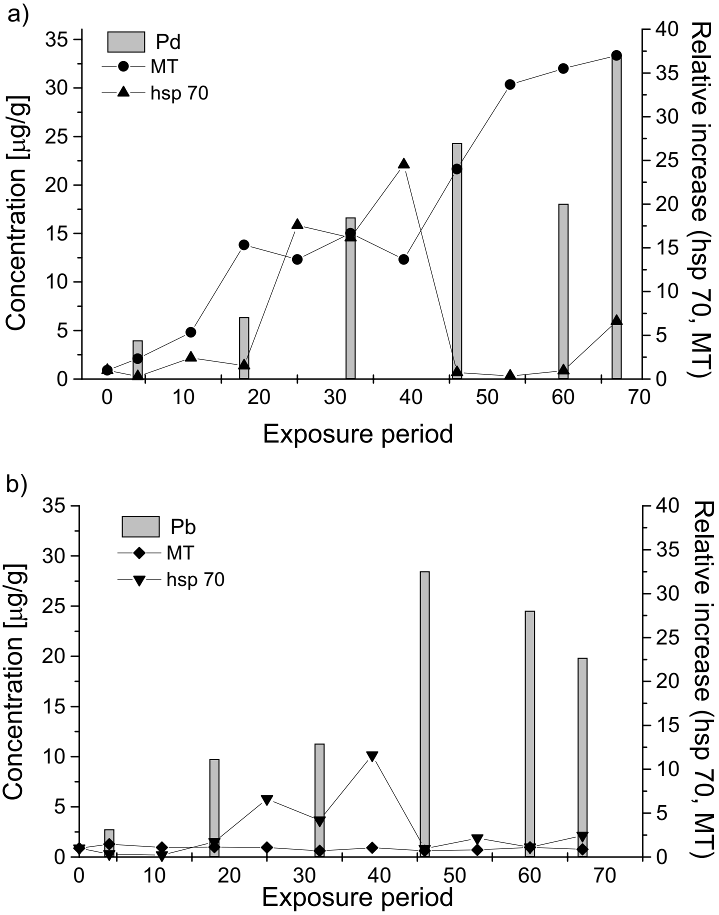

Fig. 4.1.1. Palladium (a) and lead (b) concentrations [µg/g dry weight] and relative levels of heat shock proteins (hsp70) and metallothioneins (MT) in the soft tissue of *Dreissena polymorpha* during 10 weeks of exposure to Pd(II) and Pb(II), respectively (for details see Singer et al. submitted a, b)

All groups reached maximum hsp70 concentrations at day 39 with subsequently decreasing levels (see Fig. 4.1.1). Threshold metal levels for the hsp70 induction varied among the metals and increased in the order Rh < Pd < Pb < Pt < Cd. Highest hsp70 values were found for mussels exposed to Pd, which reached a 25fold higher level than the controls, followed by Pt- and Rh-exposed mussels which showed a 19fold increase. The hsp70 levels of the mussels exposed to Cd and Pb were much lower, showing only 6fold and 12fold higher values than the control, respectively (Singer et al. submitted a). Accordingly, among the metals investigated Pd seems to have the highest potential for hsp induction due to its low induction threshold level in combination with the strong effect.

A clear increase in MT levels was also detected for those mussels which were exposed to Pt, Pd and Cd (Singer et al. submitted b). Following 10 weeks of exposure a 37-fold higher MT level was detected due to Pd exposure compared with initial values (Fig. 4.1.1). Interestingly, the accumulation of Pd was significantly ($p < 0.001$) correlated with the levels of MT (Spearman $r = 0.9643$). Only Cd, which is already known as a very efficient inducer of MT synthesis (High et al. 1996), showed with a 141-fold increase a more pronounced effect on the MT concentration. In contrast, Pb and Rh failed to show the induction of MT synthesis in *D. polymorpha.*

Similar studies investigating metal uptake and levels of hsp70 using ground catalytic material as a pollution source for exposure of zebra mussels have revealed comparable results. However, the use of particulate PGM resulted in a later onset of increasing hsp70 levels when compared with soluble metal species (Som, 2004). This might be attributed to the fact that the metals had to be taken up by an organism as a prerequisite to affect its physiological homeostasis. In exposure studies performed with PGM, soluble metals are generally taken up much easier by animals than particulate metals (see Zimmermann & Sures, in this book). However, after the particulate metals were taken up by *D. polymorpha*, they were also able to initiate the synthesis of hsp70, which are used by cells to protect themselves against toxic effects of substances.

This example shows once more that the toxicity of Pd and their compounds depends mainly on the biological availability which itself is correlated with the solubility of the substances (Moldovan et al. 2002; Zimmermann & Sures, in this book). Soluble inorganic Pd salts are much more toxic in experiments due to a faster and higher uptake rate than compounds with a lower solubility and hence a lower uptake rate.

It can be concluded from the studies reviewed here, that Pd is recognized by cells and organisms as a toxic metal. Accordingly, specific metal binding proteins (MT) are synthesized which should help to detoxify this metal. Those ions, which reach a cell before they are bound to MT or similar proteins, elicit the cellular stress response (hsp70). These proteins should help cells to avoid the collapse of their membranes and enzyme functions.

4.1.7 Conclusion

The risk of Pd and their compounds for living organisms appears to be relatively low due to their low concentrations in the environment (e.g., Gebel 2000; Rosner & Merget 2000). However, for Pd only few data are available, which are not sufficient to present a comprehensive risk assessment (IPCS 2002). Nevertheless, the clear increase of PGM contamination especially in urban habitats due to car emissions may cause an exposure of biota including man in low and chronic doses. Thus, although the risk of Pd is low for the general population, continuous environmental monitoring of this metal as well as of the other PGM in combination with studies on the toxicity of these elements is strongly recommended. From the available literature it appears that Pd is the most biologically available element among the PGM, at least concerning plants and water living animals (Hoppstock & Sures 2004, Zimmermann & Sures 2004, Zimmermann & Sures chapter in this book). These findings together with the relatively scarce results from toxicity tests should raise the question of Pd being a more potent threat to the environment and living organisms than the other PGM. This should be elucidated in the near future.

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4.2 Uptake of Palladium by the Fauna

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4.2.1 Introduction

Since 1985 the total global demand of the platinum group metals (PGM) Pt, Pd and Rh has doubled with a still increasing tendency. In 2004 the total global demand of Pd was 191 t, with 114 t being used in the autocatalyst sector (Johnson Matthey 2004). As a consequence of the growing use of Pd, elevated Pd concentrations were found in different environmental matrices such as airborne particulate matter, road dusts and soils along heavily frequented roads (summarized in e.g. Zereini and Alt 2000, Hoppstock and Sures 2004). Besides of terrestrial ecosystems, Pd is also introduced into aquatic habitats.

Depending on the age and type of the catalytic converter the emission rate of an individual car is up to 50 ng Pd per km (Moldovan et al. 2002). The platinum group metals are emitted attached to aluminium oxide particles, mainly in the oxidation status of zero or as oxides (Moldovan et al. 2002). Therefore, it may be assumed that PGM behave in an inert manner and are immobile in the environment. But solubility studies with automobile exhaust fumes and road dusts revealed that Pd emitted from cars is at least partly soluble and therefore mobile (Moldovan et al. 1999 & 2002, Palacios et al. 2000, Jarvis et al. 2001). Accordingly, the effects of increasing PGM emissions on the biosphere are more and more controversially discussed (Zimmermann and Sures 2004).

One of the main results of recent research is the proof that PGM are biologically available. As biological availability is one of the most decisive factors determining the toxicological potential of xenobiotics, this information is very important to evaluate the possible threat of the noble metals to ecosystems. Unfortunately, there are only few studies on the biological availability of Pd since the determination of Pd is usually more challenging than the analysis of Pt and Rh. Furthermore, metal determination in animal tissues often requires very sensitive techniques as the sample amount of animals is generally restricted. This chapter summarizes the limited data on the biological availability, uptake and accumulation of Pd for animals and emphasizes the lack of knowledge where research has to be done.

4.2.2 Biological availability to terrestrial animals

Investigations on the biological availability of Pd to terrestrial animals are very scarce as e.g. exposure studies are generally more easily performed with aquatic animals than with terrestrial species.

In preliminary exposure studies on the toxicity and metabolism of $PdCl_2$ the retention, tissue distribution and excretion of Pd was determined in rats following oral, intravenous, intratracheal and inhalative exposure (Moore et al. 1975). For example, after intravenous exposure of pregnant rats, Pd was found (in order of decreasing Pd content) in kidney, liver, placenta, ovary, lung, bone and blood of the maternal rats and in the fetus.

Concerning field studies, analysis of feathers of peregrine falcons and sparrowhawks from 1917-1999 gave evidence for increasing environmental Pd concentrations (Jensen et al. 2002). However, laser ablation profiles of PGM demonstrated that the metal contaminations of the feathers consisted almost exclusively of externally attached PGM-containing particles, with little evidence of internally deposited PGM (Ek et al. 2004a). Nevertheless, Pd was also detected in eggs (without shells), blood, liver and kidney of peregrine falcons as well as in eggs of sparrowhawks in Sweden (Ek et al. 2004b).

Due to this limited information, field studies as well as laboratory investigations on the biological availability of Pd to terrestrial animals are needed.

4.2.3 Biological availability to aquatic animals

In recent years the biological availability of Pd to aquatic animals has been investigated in several laboratory experiments but only very few field studies.

Uptake and accumulation of Pd by aquatic organisms in the laboratory was demonstrated for the isopod *Asellus aquaticus* (Moldovan et al. 2001), the mussel *Dreissena polymorpha* (Sures et al. 2002a & b, Zimmermann et al. 2002, 2003 & 2005a) and the fish species *Anguilla anguilla* (Sures et al. 2001, Zimmermann et al. 2005b) and *Barbus barbus* (Sures et al. 2002a & 2005). The biological availability of Pd to aquatic animals was shown in experimental studies using soluble metal species (Moldovan et al. 2001, Zimmermann et al. 2003), ground catalytic converter materials (Moldovan et al. 2001, Sures et al. 2002a & 2005, Zimmermann et al. 2003, 2005a & b) or sediments of urban rivers, road and tunnel dusts (Moldovan et al. 2001, Sures et al. 2001, Zimmermann et al. 2002).

Besides of free living organisms, intestinal worms parasitizing fish were found to accumulate Pd to a remarkable degree as it is known for "common" heavy metals such as Pb or Cd (reviewed in Sures 2003 & 2004).

Following exposure to catalyst material the acanthocephalans *Pomphorhynchus laevis* and *Paratenuisentis ambiguus* demonstrated 12 and 4 times higher Pd levels as compared with the liver of their fish hosts, barbel and eel, respectively (Sures et al. 2005, Zimmermann et al. 2005b). Therefore, the use of fish parasites as accumulation indicators for metal contaminations in aquatic ecosystems is discussed (see Thielen et al., in this book).

In addition to laboratory exposure studies, Moldovan et al. (2001) analysed Pd in *Asellus aquaticus* from an urban river receiving traffic input from Göteborg, Sweden, and found levels (related to dry weight) of 155.4 ± 73.4 ng/g Pd which were about four times higher as compared with the Pd concentrations determined in the river sediment. As no PGM were identified in the river water the authors suggested that the main uptake occurred from the metal content in the sediment. Furthermore, in context of an exposure study Sures et al. (2005) analysed Pd in barbels (*Barbus barbus*) caught in the river Danube near Budapest, Hungary. After maintaining the fish for 28 days in clean water, the mean Pd levels (related to fresh weight) were determined as 7 ng/g for liver, 1 ng/g for kidney and 0.3 ng/g for gill. The parasitic worm *Pomphorhynchus laevis* found in the intestine of the fish contained 0.5 ng/g Pd.

4.2.4 Factors affecting bioaccumulation

As it is known for common heavy metals, also the uptake of Pd by animals is dependent on various factors such as exposure concentration, exposure period, test species, way of metal application (e.g. oral, intravenous, inhalative or aqueous) and metal speciation. Additionally, in aqueous systems the water chemistry is an important parameter affecting the metal speciation and thereby the biological availability.

The variation in the accumulation capacity of Pd for different test organisms and the metal distribution within the animals is discussed in the chapter of Thielen et al.

Exposure experiments were performed with mixed as well as with single metal sources. This leads to the question whether interactions among the metals occur which may influence metal uptake. Accordingly, Moldovan et al. (2001) exposed *Asellus aquaticus* to mixed and individual PGM standard solutions and found no competition between Pt, Pd and Rh in respect of their bioaccumulation. Similar results were obtained from experiments with zebra mussels (Zimmermann 2002).

As expected, the Pd concentrations in freshwater isopods and zebra mussels rose with increasing exposure concentrations in the tank water (Moldovan et al. 2001, Zimmermann 2002). But the bioaccumulation factor (BCF, ratio between the Pd level in the test organism and the ambient water) was not dependent on the exposure concentration (Moldovan et al. 2001).

In experiments with soluble PGM salts the Pd levels in the soft tissue of zebra mussels reached an accumulation plateau after approximately three days of exposure whereas in studies with ground catalytic converter material the PGM levels in the bivalves increased over the whole exposure period of 18 weeks (Zimmermann 2002, Zimmermann et al. 2005a). Accordingly, the bioaccumulation of PGM by bivalves is dependent on the exposure period and the metal speciation. In mussel experiments with different metal sources BCFs were calculated not taking into account whether the metals are dissolved or particle-bound. The highest concentration factors were found for soluble metal salts, followed by catalyst material and road dust (Fig. 4.2.1). The differences in the bioaccumulation of PGM from road dust and catalyst material indicates that transformation processes take place in the environment.

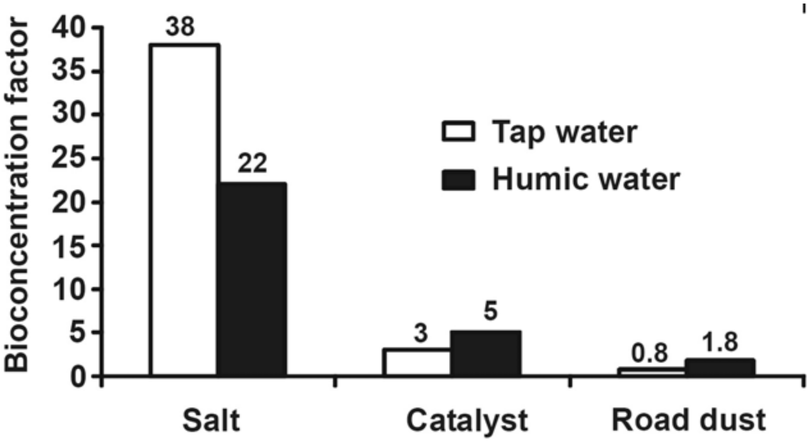

Fig. 4.2.1. Bioconcentration factors (BCF = $c_{\text{mussel tissue}}/c_{\text{water, applied}}$) for the accumulation of Pd by *Dreissena polymorpha* exposed to tap water and humic water, respectively, containing soluble PGM salts, catalyst material or road dust (for details see Zimmermann 2002, Zimmermann et al. 2002 & 2005a)

Investigations on the influence of the uptake pathway were performed with terrestrial and aquatic animals. Following exposure to $PdCl_2$, the highest whole-body retention of Pd in rats was found after intravenous administration, followed by intratracheal, inhalative and then oral administration; the enteral absorption of Pd after oral application was less than 0.5% (Moore et al. 1975).

In exposure studies on the Pd uptake by aquatic animals the metal is generally added to the ambient water of the test species, so that the route of uptake remains unclear. The pathway certainly depends on whether the metals are applied in soluble form or as particles. Especially in the case of particles, the feeding behaviour of the test organism has a significant influence on the uptake and accumulation. For example, mussels are known to take up dissolved as well as particulate metals (Roditi and Fisher 1999) as they can capture particulate matter by their gills and select particles in their stomach (Ward and Shumway 2004). Accordingly, the uptake of Pd by zebra mussels was demonstrated in exposure studies using soluble Pd salt as well as particle-bound Pd from catalyst material or road dust (Zimmermann 2002, Zimmermann et al. 2002 & 2005a). In contrast, freshwater fish generally take up dissolved metals from the ambient water via their gills (Gunkel 1994). Consequently, particle-bound Pd is most probably not available for fish via this route. But Pd uptake by fish was found in exposure studies with soluble species as well as with particulate Pd from catalyst material or road dust (Sures et al. 2001 & 2005, Zimmermann et al. 2005b). This leads to the assumption that solubility processes play a significant role for the biological availability of particulate Pd to fish. However, the aqueous solubility of metals depends on the water chemistry.

The effect of the water chemistry on the biological availability of PGM was demonstrated in exposure studies with catalyst material and road dust, respectively, showing a clearly higher Pd uptake in mussels maintained in humic water as compared with tap water (Zimmermann et al. 2002 & 2005a). In contrast to the experiments with particle bound PGM, studies with soluble Pd salts revealed contradictory results with higher bioaccumulation in tap water than in humic water (Fig. 4.2.1). This discrepancy between particulate and soluble Pd species may be explained by the formation of Pd complexes with humic substances in combination with the assumption that these complexes are biologically available to mussels, but to a lower degree as compared with free Pd ions. There are some evidences for this hypothesis. Wood et al. (1994) demonstrated in solubility experiments, that the presence of fulvic acids prevents precipitation of Pd over a wide pH range. Additionally, investigations on the effect of humic acid on the uptake of Cd(II) by zebra mussels revealed a decrease in the metal uptake rate due to the presence of humic acid in the water (Voets et al. 2004). However, Voets et al. (2004) found also evidences, that zebra mussels are able to consume humic acid from water and consequently the humic acid complexed metals.

4.2.5 Uptake of palladium as compared with other metals

A comparison of the uptake of Pd with that of Pt and Rh demonstrate that all three noble metals react in different manners. Using PGM standard solutions as metal source, Moldovan et al. (2001) found in short-time (24 h) exposure studies with *Asellus aquaticus* the highest bioaccumulation for Pd, followed by Pt and Rh. In contrast, in experiments with zebra mussels also exposed to PGM standard solutions over several weeks, Pd was accumulated to a lower degree than Pt (Singer et al., submitted). The discrepancy may be due to the use of standard solutions from different manufacturers with probably varying metal speciation. Furthermore, both studies differed significantly in the exposure period and the test organism used. In comparison, also in other studies with zebra mussels exposed to PGM salts ($PtCl_4$, $PdSO_4$ and $RhCl_3$) the bioaccumulation decreased in the order Pd(II)>Pt(IV)>Rh(III) (Zimmermann & Sures submitted).

Using catalyst material for exposure, there were only slight differences in the accumulation of Pt, Pd and Rh by *D. polymorpha* indicating that the metals were taken up as particles (Zimmermann et al. 2005a). Moldovan et al. (2001) found similar results in experiments with *A. aquaticus* exposed to car catalyst powder. In contrast, different uptake rates for the three PGM were found in exposure studies with environmental samples such as road or tunnel dust and river sediments (Moldovan et al. 2001, Zimmermann et al. 2002). In studies with zebra mussels using road dust as PGM source, the highest concentration factors among the PGM were determined for Pd, followed by Pt and Rh (Fig. 4.2.2). The different bioaccumulation determined with environmental samples may be explained by environmental transformation processes of the PGM. There are some evidences from experiments on the aqueous solubility of PGM and from field studies on the PGM distribution in dust and sediment samples from the vicinity of roads that Pd is more mobile in the environment than Pt and Rh (e.g. Fuchs and Rose 1974, Claus et al. 1999, Moldovan et al. 1999, Jarvis et al. 2001, Ek et al. 2004c). Furthermore, it could be demonstrated for zebra mussels exposed to catalyst material that the enhancing effect of humic water on the PGM accumulation was highest for Pd as compared with Pt and Rh (Zimmermann et al. 2005a).

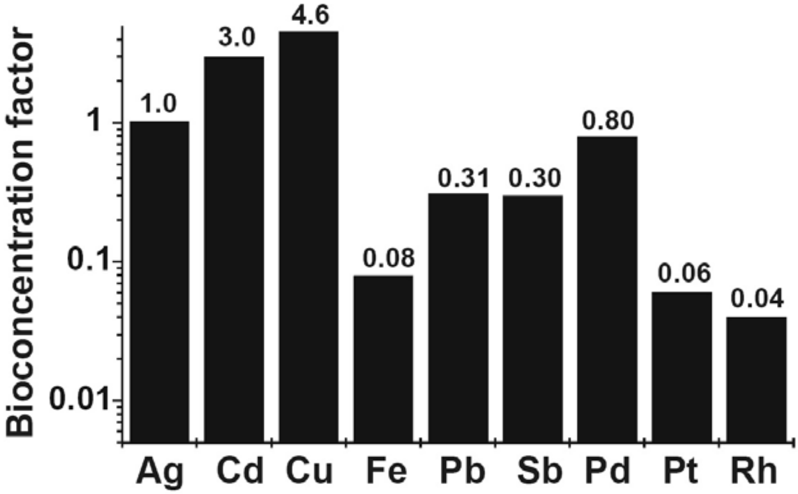

Fig. 4.2.2. Bioconcentration factors (BCF = $c_{\text{mussel tissue}}/c_{\text{water, applied}}$) for the accumulation of Pd as compared with other heavy metals by *Dreissena polymorpha* exposed to tap water containing road dust over 26 weeks (for details see Zimmermann et al. 2002)

Additionally, the accumulation of Pd in zebra mussels exposed to road dust was compared with that of other heavy metals (Fig. 4.2.2). The bioconcentration factor of Pd was about 6 times lower, but 10 times higher as compared with the essential metals Cu and Fe, respectively. Compared with the formerly traffic relevant Pb the Pd accumulation was about 3 times higher. Cd which is known as toxic metal exceeded the bioconcentration factor of Pd only by a factor of less than 4.

4.2.6 Conclusions

Although there is a cumulative increase in the environmental Pd contamination mainly due to rising traffic densities of automobiles with catalytic converters, less than 20 publications deal with the biological availability, uptake or bioaccumulation of Pd for animals. This low number of studies may be due to the high requirements of the (ultra) trace analysis of Pd in biological material. Therefore, we urgently need reliable techniques for the Pd analysis which can be routinely used in conventional analytical laboratories.

Furthermore, most reports refer to laboratory studies with aquatic animals and consequently, there is a great lack of field data and investigations on the uptake of Pd by the terrestrial fauna. Nevertheless, the biological availability of soluble Pd species and traffic related Pd to animals has been doubtlessly proved. In addition, experimental studies revealed that environmental transformation processes, e.g. due to the presence of humic substances, can even enhance the uptake of particulate Pd by animals. But we are still at the very beginning to understand the uptake mechanisms or the factors affecting the biological availability of Pd. Research has to be urgently done in this field since toxic effects (see Sures et al., in this book) generally imply the metal uptake by organisms and this information is very important for a responsible evaluation of the environmental risk of Pd.

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4.3 Biomonitoring of Palladium in the Environment Using Different Accumulation Indicators

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4.3.1 Introduction

Palladium and its chemical compounds are primarily used by autocatalyst manufacturer, the electrical industry, dental laboratories, and the chemical and jewellery industry. Whilst the demand of most sectors remained at the same level during the last 20 years the demand of the autocatalyst sector has increased more than tenfold (Hoppstock and Sures 2004) due to the change-over from Platinum/Rhodium-converters to Palladium/Rhodium-converters in the last decade (Helmers et al. 1998).

The fact that Pd emitted by catalytic converters shows a higher water solubility and chemical mobility in the environment (Beyer et al. 1999, Claus et al. 1999) than Pt and Rh leads to the assumption that also the biological availability of this noble metal is higher. This assumption has been confirmed in a number of laboratory studies (see Zimmermann and Sures, in this book). Furthermore, the uptake of Pd by plants and animals has been demonstrated in field studies (reviewed in Ek et al. 2004a, Zimmermann and Sures 2004). Nevertheless, only very scarce information exists about the distribution of Pd in the biosphere, in particular in the fauna. For the assessment of the environmental risk of Pd we have to know the status of Pd contamination in the environment.

To evaluate the exposure of natural ecosystems to Pd, environmental indicators (bioindicators) as a direct or indirect measure of environmental quality are used. Bioindicators can be used either as effect indicators or as accumulation indicators on the level of single species, populations or natural communities. Effect indicators can provide valuable information about the chemical state of their environment through changes of their physiology and/or behaviour (Sures 2004). Effect indication in its widest sense is also possible on cellular and subcellular levels. Then we talk about biomarkers which are defined as “a change induced by a contaminant in the biochemical or cellular components of a process, structure or function that can be measured in a biological system" (NRC 1989). Until now, there is only little information available on effect indicators or biomarkers for platinum group metals (PGM). However, recent exposure studies with zebra mussels indicated that the induction of heat shock proteins and metallothioneins are promising parameters for effect indication (see Sures et al. in this book).

In contrast to effect indication, more investigations are related to the accumulation potential of different organisms for Pd. Consequently, this chapter focuses on the use of different organisms as accumulation indicators with emphasis on animals. The ability to concentrate environmental pollutants inside their tissues makes accumulation indicators suitable for gaining information about the status and trends of environmental pollutants in the habitat investigated. The use of accumulation indicators is advantageous compared with direct analysis (e.g. in water or sediments) because only the fractions that are biologically available are taken up and concentrated by the test organism. Furthermore, accumulation indicators are able to integrate pollutants over time. Finally, the pre-concentration in sentinels enables the detection of very low concentration of pollutants in ecosystems and can facilitate the chemical analysis. In respect of Pd, this point is of high interest as the (ultra) trace analysis of Pd is still often challenging.

4.3.2 Plants

The use of plants as accumulation indicator for Pd implies that the plants are able to accumulate the metal. Laboratory as well as field studies demonstrated this capacity for a number of plant species (reviewed in Ravindra et al. 2004, Ek et al. 2004a, Zimmermann and Sures 2004).

Concerning aquatic plants bioaccumulation of Pd was demonstrated for the water hyacinth *Eichhornia crassipes* (Farago and Parsons 1994). As this study was performed with soluble Pd salts, no information is available whether this plant is also able to accumulate particulate Pd as emitted from automobile catalysts. Therefore, further tests have to be conducted to assess the accumulation potential of aquatic plants for traffic emitted Pd.

In contrast to aquatic plants, more publications report on the Pd accumulation by terrestrial plants. Using soluble Pd salts accumulation of Pd was found for the grass *Lolium multiflorum* (Lesniewska et al. 2004), endive *Cichorium endivia* (Alt et al. 2002) and lettuce *Lactuca sativa* (Weber et al. 2004). However, since Pd is mainly emitted in particulate form, emphasis of this chapter lays on investigations dealing with traffic related Pd and on field studies. In greenhouse experiments the transfer coefficient of spinach, cress, phacelia and stinging nettle cultivated on soils collected from the vicinity of a German highway decreased from Pd > Pt > Rh and ranged between the values of immobile to moderately mobile elements such as Cu and Ni (Schäfer et al. 1998). In this study phacelia and stinging nettle showed a slightly higher Pd transfer from the soil than spinach and cress.

In contrast to laboratory experiments, in field studies an overestimation of the bioaccumulation is possible due to the deposition of metals on the plant surfaces. For example, washed leaves of dandelion (*Taraxacum officinale*) and plantain (*Plantago lanceolata*) showed 2-3 times lower PGM concentrations than unwashed samples (Djingova et al. 2003). Consequently, in biomonitoring studies with shoots of terrestrial plants it must be decided whether only the fraction which was absorbed or also the deposited metals should be investigated. This problem could be avoided by the analysis of roots which generally seemed to accumulate Pd to a higher degree than shoots (Lesniewska et al. 2004). But according to Lesniewska et al. (2004) also for roots adsorbing effects of Pd on the surface can not be excluded.

To use terrestrial plants as accumulation indicators there are two possibilities for sampling: (1) plant samples are collected in the environment (passive monitoring) and (2) plants cultivated under standardized conditions are exposed for a certain period at the site of interest and then sampled (active monitoring). Until now, in most field studies passive monitoring of Pd was performed investigating pine needles, leaves of grass (not further characterized), annual ryegrass (*Lolium multiflorum*), dandelion (*Taraxacum officinale*) and plantain (*Plantago lanceolata*), moss (*Rhytidiadelphus squarrosus*) and mushrooms (*Vascellum pratense*) (Fuchs and Rose 1974, Schuster et al. 2000, Djingova et al. 2003, Dongarra et al. 2003).

One of the best established plants for active monitoring of airborne pollutants is the widespread annual ryegrass (*Lolium multiflorum*) which is used as standardized grass culture (Peichl et al. 1994, Wäber et al. 1996). The accumulation capacity of this grass for Pd was demonstrated in greenhouse experiments (Lesniewska et al. 2004) as well as in field studies (Djingova et al. 2003, Abbas et al. 2002). For example, grass samples from cultures grown along the heavily frequented Highway A5 in Germany showed Pd levels of 2-3 µg/kg. (Abbas et al. 2002).

4.3.3 Fauna

As compared with plants biomonitoring of Pd using animals is more delicate due to ethical problems. The uptake and bioaccumulation of Pd by aquatic and terrestrial animals is described in detail in the chapter of Zimmermann and Sures. This chapter compares the accumulation capacity of different animals and in the case of vertebrates also that of different organs/ tissues within the test organism.

For aquatic ecosystems the freshwater isopod *Asellus aquaticus*, the zebra mussel *Dreissena polymorpha* and the fish species *Anguilla anguilla* and *Barbus barbus* may be promising accumulation indicators for Pd due to their potential to accumulate PGM. Each test organism has its pros and cons.

Asellus aquaticus is a widespread species found in unpolluted as well as in contaminated eutrophic waters and showed in exposure studies and field investigations a high accumulation of Pd (Moldovan et al. 2001). However, it is known that crustaceans accumulate metals in their exoskeleton which is moulted frequently (Rauch and Morrison 1999). Therefore, the metal content in the crustaceans depends on their moulting status (Rauch and Morrison 1999). Furthermore, analysis of *A. aquaticus* before and after depuration demonstrated that significant amounts of metals are adsorbed onto the exoskeleton and are not metabolized by the organism (Rauch and Morrison 1999).

The Zebra mussel, *Dreissena polymorpha*, is one of the best established bioindicators worldwide. This bivalve can be used as an accumulation indicator for organic xenobiotics as well as for heavy metals (Sures et al. 1999). Recent exposure studies with soluble salts, catalyst materials and road dust also demonstrated a high accumulation potential for Pd (see Zimmermann and Sures, in this book). In these studies, mussels were transferred to clean water for 2 days after exposure to avoid contamination while sampling and to remove particles from the gill and the intestine of the mussels according to Roditi and Fisher (1999). Furthermore, the zebra mussel meets the criteria for passive and active monitoring. But especially in the case of active monitoring it should be considered that *D. polymoroha* is originally an invader from the Ponto-Caspian and not a native species in central Europe (Bij de Vaate et al. 2002). Although the zebra mussel shows meanwhile a widespread distribution throughout Europe and North America, an introduction to ecosystems which lack this bivalve (e.g. lakes, ponds, rivers) should be avoided.

Beside of invertebrates, also fish are able to bioconcentrate Pd in various tissues. Fig. 4.3.1 shows the Pd distribution within eel (*Anguilla anguilla*) and barbel (*Barbus barbus*) both exposed to catalyst material. As it is known for other heavy metals, generally kidney and liver are the typical target organs of Pd accumulation. Additionally, the intestinal wall can accumulate Pd, but to a lower degree than kidney and liver. Only a low Pd accumulation was found in muscle tissue.

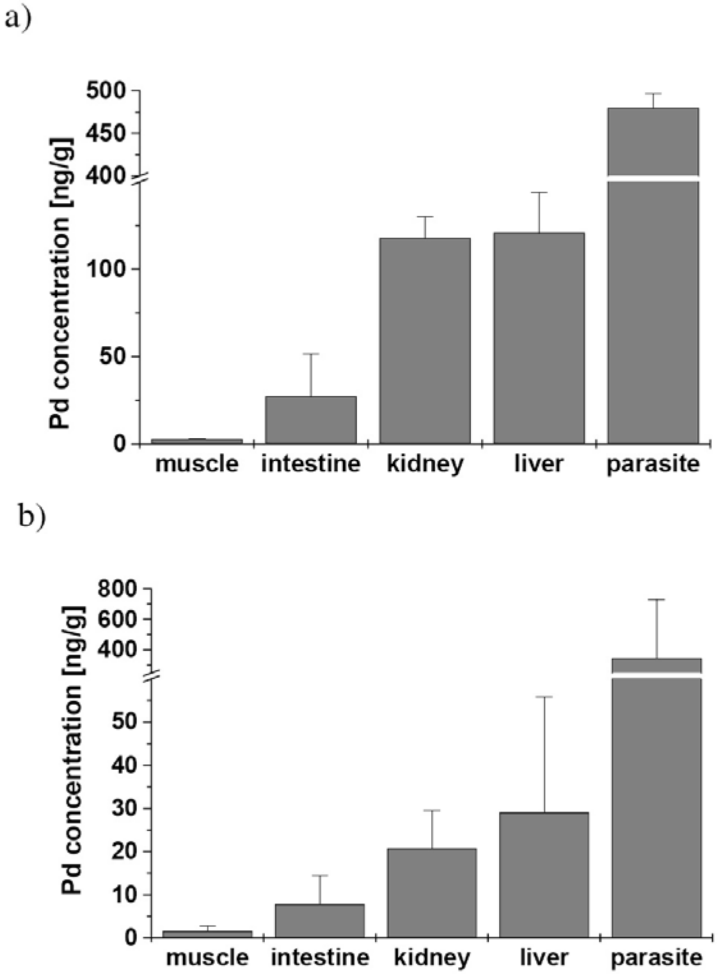

Fig. 4.3.1. Pd distribution in (a) eels (*Anguilla anguilla*) infected with *Paratenuisentis ambiguus* and (b) barbels (*Barbus barbus*) infected with *Pomphorhynchus laevis* following exposure to ground catalyst material (for details see Sures et al. 2005 and Zimmermann et al. 2005a).

In comparison with the fish tissues, a far higher Pd accumulation was determined in the intestinal parasites sampled in eels and barbels (Fig. 4.3.1). The Pd concentration in *Paratenuisentis ambiguus* was 4 times higher than in kidney or liver of eel. Similarly, *Pomphorhynchus laevis* showed 17 and 12 times higher Pd levels than kidney and liver of barbel.

Both parasites are acanthocephalans, parasitic worms which live as adults in the intestine of vertebrates (Taraschewski 2000). Due to their parenteral nutrition via their body surface, metals analysed in these helminths are definitely metabolized. Beside of Pd, the exceptional accumulation potential of this helminth group was demonstrated for numerous metals including Pt, Rh, Cd, Pb etc. and consequently the use of acanthocephalans as accumulation indicators gains increasing interest (reviewed in Sures 2003 and 2004).

Although the exposure conditions differed from experiment to experiment, a rough comparison of the accumulation potential of the different test organisms is possible by using bioconcentration factors (BCF, ratio between the Pd level in the test organism and the ambient water) (Table 4.3.1).

Table 4.3.1 demonstrates that exposure studies with catalyst material were performed for all test organisms. Comparing these studies and taking into account that there is approximately a factor of 10 between dry weight and fresh weight, the BCFs decreased in the order: *A. aquaticus* > *P. laevis* > *P. ambiguus* > *D. polymorpha* > fish liver and fish kidney.

However, since such a high uptake of particulate Pd within 24 h is dubious, the BCF of *A. aquaticus* is most probably overestimated due to adsorption of catalyst particles on the body surface or due to metal particles in the intestine which were not metabolized. These uncertainties can be excluded by using parasites. This appears to be even more reasonable as a previous study on the uptake and accumulation of Pb and Cd showed that acanthocephalans had 5 to 11 times higher metal concentrations than *A. aquaticus* (Sures et al 1994, Sures & Taraschewski 1995).

In contrast to aquatic habitats, far less information is available on the use of animals as bioindicators in terrestrial ecosystems. Probably feathers of birds may be useful to detect airborne Pd similarly taking into account that the Pd levels measured are predominantly external (Jensen et al. 2002, Ek et al. 2004b). For example, in feathers of three raptor species a clear temporal increase of Pd could be detected from 1917 to 1999 in Sweden (Jensen et al. 2002). To investigate the biological available Pd fraction in terrestrial environments, inner tissues e.g. of birds are more reliable. For example, in a field study Pd was detected in eggs, blood, liver and kidney of peregrine falcons as well as in eggs of sparrowhawks (Ek et al. 2004c).

As already discussed for aquatic systems, also intestinal parasites of terrestrial vertebrates e.g. rats are known to bioconcentrate metals to a high degree (reviewed in Sures 2004). However, it has to be proofed if also PGM are accumulated by these parasites. Nevertheless, rats infected with intestinal worms are worldwide distributed in particular in polluted, urban areas and may be very promising bioindicators for terrestrial ecosystems.

Table 4.3.1. Bioconcentration factors (BCF) for Pd determined in exposure studies with different test organisms and metal sources (DW: dry weight, FW: fresh weight)

Test organism	Sample	Metal source	Exposure period	BCF	Reference
A. aquaticus	Whole body, DW	standard solution	24 h	150	Moldovan et al. 2001
		Catalyst material	24 h	36	Moldovan et al. 2001
D. polymorpha	Soft tissue, DW	$PdSO_4$	4 weeks	38	Zimmermann and Sures, submitted
		Catalyst material	6 weeks	2.7	Zimmermann et al. 2005b
		Road dust	26 weeks	0.8	Zimmermann et al. 2002
A. anguilla	Liver, FW	Catalyst material	6 weeks	0.121	Zimmermann et al. 2005a
	Kidney, FW			0.119	
B. barbus	Liver, FW	Catalyst material	4 weeks	0.123	Sures et al. 2005
	Kidney, FW			0.088	
P. ambiguus	Whole body, FW	Catalyst material	6 weeks	0.482	Zimmermann et al. 2005a
P. laevis	Whole body, FW	Catalyst material	4 weeks	1.47	Sures et al. 2005

4.3.4 Conclusion

The cumulative increase of the PGM in the environment, the unexpected high biological availability and bioaccumulation, especially for Pd, as well as the unknown toxicological and ecotoxicological potential makes a monitoring of these elements in the environment indispensable (Zimmermann &

Sures 2004). Accordingly, powerful and reliable bioindicators are necessary. In the aquatic environment *Asellus aquaticus*, the zebra mussel (*Dreissena polymorpha*), the eel (*Anguilla anguilla*) and barbel (*Barbus barbus*) turned out to be suitable accumulation indicators, as all these organisms were able to accumulate Pd. Beside these free living organisms in particular acanthocephalans show remarkable accumulation capacities. The need of these “new” and powerful sentinels can be explained by their ability to detect and assess the distribution of pollutants, even in remote areas where concentrations are very low such as the Antarctica (see Sures and Reimann 2003). In the terrestrial environment plants (e.g. *Lolium multiflorum*) can serve as bioaccumulation indicators for Pd, but deposition and adsorption effects must be considered as mentioned above. Further field studies and more investigations with relevant environmental concentrations are necessary to established plants and animals as bioaccumulation indicators for routine monitoring of the PGM. Also studies dealing with terrestrial vertebrates including their parasitic worms are of highest interest, as only few data about bioaccumulation exists in this area. Acute risks and effects on ecosystems due to palladium seem not to exist, but as chronic effects of PGM, especially of the very mobile Pd, can not be excluded a monitoring of this element with biological bioindicators is advisable.

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4.4 Biomonitoring of Pt and Pd with Mosses

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4.4.1 Introduction

Platinum (Pt), palladium (Pd), and rhodium (Rh) belong to the rarest element group in the lithosphere and biosphere. Their background values lie in the range of 0.1 $ng{\cdot}g^{-1}$ to 1 $ng{\cdot}g^{-1}$ (Wedepohl, 1995). However, since the introduction of Pt-containing auto catalyst converters during the 1970's in the USA and later in Japan and Europe, their concentrations in the environment, especially in the roadside environment, have increased rapidly (Lustig, 1997). Retrospective studies on airborne dust samples (Zereini et al. 1997) and ancient ice (Barbante et al. 2001) have facilitated the assessment of the environmental dispersion of these platinum group elements (PGE). Increases in the concentration of PGEs in the environment have been documented in numerous countries and matrixes (Ravindra et al. 2004).

As a result, there is now a growing concern on the ecological and human risk of increasing concentrations of PGE in the environment. There have been several passive biomonitoring studies to investigate the bioaccumulation of platinum in animals and plants. An experiment of active biomonitoring of platinum has been performed using grass cultures (Dietl et al. 2000). Palladium bioaccumulation has been less documented as stated by Lustig and Schramel (2000).

Moss analyses have been utilized successfully in the environmental biomonitoring of heavy metal atmospheric deposition studies during the past 30 years (e.g. Steinnes, 1995). Both active (using transplanted moss) and passive (using endogenous) monitoring methods have been developed and applied to the monitoring of inorganic and organic pollutants. The following sections examine the feasibility of using mosses to assess Pt and Pd pollution in the region of Paris, France, and compare the obtained data with those published on PGE biomonitoring using grass.

4.4.2 Literature overview

Since the increase of the PGE concentrations was recognized in the environment by pioneer German studies, there has been an intense discussion on the levels of these elements in the environment, their pathway from dust to plants and their ecotoxicology.

After several years of development and improvement of analytical methods, PGE levels were measured in a wide range of plant species and sites. Table 4.4.1 summarizes the literature data for PGE concentrations in grass and moss. Additional data for plants can be found in Ravindra et al. (2004).

The PGE concentrations in plants contaminated by road traffic are highly variable from a study to another. At least, in the same study, when the plant species and the analytical procedure are identical, and the sampling site comparable, the elemental concentration or the concentrations ratio are close (Ely et al. 2001; Vanhaecke et al. 2002). When multiple species are investigated (Alt et al. 1997; Djingova et al. 2003; Niemelä et al. 2004), the concentration varies in one order of magnitude. Mosses exhibit the highest PGE concentrations, while the elemental ratio observed is comparable to those observed for dandelion or plantain. The main difficulty with mosses is to sample them in open and polluted spaces very close to road. The rye grass *Lolium multiflorum*, easy to find along roads, appears to fairly concentrate the PGE. The highest Pt/Pd ratios are found for *Lolium multiflorum* because of very low Pd concentration observed for that species (Djingova et al. 2003). Djingova et al. (2003) concluded from a study of different plant species collected in the same site that the PGE accumulation behaviour of plants was similar to those of heavy metals and toxic elements. Similar accumulation trends were seen for PGE and traffic-related elements: Pb, Ce, Zr, La, Ni, Zn, Cu (Ely et al. 2001; Djingova et al. 2003; Niemelä et al. 2004).

Table 4.4.1. Literature overview: concentrations of Pt, Rh and Pd in grass and moss (µg.kg^{-1} of dry weight).

Sample	Year	Sampling site	Distance from road (m)	Pt	Rh	Pd	Pt/Rh	Pt/Pd	Data source
Grass	1995	Highway, Germany		5		0.6		8.3	Schäfer et al. 1998
Washed[a] grass		Indiana Toll road, US	0	1.23±0.27	0.10±0.02	1.03±0.23	12.3	1.2	Ely et al. 2001
Grass		Indiana Toll road, US	0	1.73±0.44	0.11±0.04	1.29±0.25	15.7	1.3	
Washed[a] grass		Indiana Toll road, US	18	1.69±0.19	0.10±0.03	0.97±0.37	16.9	0.9	
Grass		Indiana Toll road, US	18	1.41±0.68	0.12±0.05	1.44±0.30	11.8	1.0	
Moss (*Rhytidiadelphus squarrosus*)	1999	Saarbruecken, Germany		30±2	5.4±0.5	2.4±0.3	5.6	12.5	Djingova et al. 2003
Dandelion (*Taraxacum officinale*)				5.4±04	2.2±0.3	0.83±0.15	2.5	6.5	
Plantain (*Plantago lanceolata)*				3.6±0.5	1.3±0.4	0.45±0.18	2.8	8	
Mushrooms (Vascellum pratense)				5.9±0.6	0.5±0.1	0.2±0.1	11.8	29.5	
Dandelion (Taraxacum officinale)		Highway A-1, Germany	1	30±1	7.0±0.6	3.1±0.4	4.3	9.7	
Plantain (*Plantago lanceolata*)				10.1±0.5	3.4±0.5	2.1±0.2	3.0	4.8	
Ryegrass (*Lolium multiflorum*)				4.6±0.3	2.2±0.4	0.10±0.03	2.1	46	

Table 4.4.1. **(cont.)** Literature overview: concentrations of Pt, Rh and Pd in grass and moss (μg.kg^{-1} of dry weight)

Dandelion (*Taraxacum officinale*)		Highway A-61, Germa	1	11.5±0.8	3.0±0.2	1.5±0.4	3.8	7.7	
Ryegrass (*Lolium multiflorum*)				5.8±0.4	2.1±0.3	0.10±0.03	2.8	58	
Dandelion (*Taraxacum officinale*)		Road B-262, Germany	1	6.4±0.5	2.0±0.3	0.9±0.1	3.2	7.1	
Plantain (*Plantago lanceolata*)				4.0±0.3	0.5±0.1	1.1±0.2	8.0	3.6	
Moss (*Pleurozium schreberi*)	2003	12500 v./day Oulu, Finland	10	27.4±5.4	4.6±0.6		6.0		Niemelä et al. 2004
		29000 v./day	3	21.9±3.4	3.6±0.4		6.1		
		29500 v./day	12-15	6.4±0.5	1.2±0.1		5.3		
		43000 v./day	9	14.7±3.5	3.7±0.2		4.0		
Dandelion (*Taraxacum vulgare*)		43000 v./day	2	1.2±0.3	<0.3		> 4		
Grass (*Calamogrosis sp.*)			1	1.7±0.3	0.7±0.1		2.4		

[a] washedwith ethanol

Several authors except Ely et al. (2001) noticed the sharp decrease in PGE concentrations when sampling distance from road edge increased. As the plants are usually unwashed, the concentrations should be interpreted as a sum of material deposited on leaves and PGE incorporated. Dust deposition seems to be the main contamination source. Nevertheless, for grass (species not specified), the washing with ethanol was ineffective to change the PGE concentration (Ely et al. 2001). This is probably due to the relative low ability of grass to accumulate dust conversely to mosses.

The sampling is usually done after a dry period (Helmers and Mergel, 1998; Djingova et al. 2003) because rain may reduce PGE concentration by washing leaves. The soil-to-plant transfer of Pt has been measured by several authors (Alt et al. 1997; Lustig et al. 1997; Djingova et al. 2003). The transfer of Pd from soil to plant is considered to be more effective because of higher solubility of emitted species, compared to Pt and Rh species (Schäfer et al. 1998; Amosse and Delbos, 2002).

4.4.3 Passive and active Pt and Pd biomonitoring with mosses in Paris area

Materials and methods

The analytical procedure used for this work is described briefly in the following. Open-air ashing was used for sample decomposition although microwave-based methods are preferred (e.g. Vanhaecke et al. 2002; Niemelä et al. 2004). Prior to ICP-MS analysis, a chemical separation was necessary to eliminate interfering elements (Cu, Y and Zr).

Reagents

The stock solutions (1000 µg.ml-1) of Pt and Pd were provided by Carlo Erba, and Spex, respectively. An internal standard solution containing 1000 ng.ml^{-1} In and Re was prepared by mixing single element solutions (Spin, and Teknolab, respectively) in 10% HNO_3. Nitric acid (65%) and HF (40%) were provided by Prolabo, (Normatom quality), and 36% HCl by Labosi, (analytical grade). Ultra-pure water used in the experiments (18.2 MΩ-cm resistance) was provided by the alfa-Q Millipore, water purification system. Both thiourea and Amberlyst A-26 were analytical grade (Carlo Erba). The resin was received in the Cl^{-1} ionic form and has an exchange capacity of 4.4 mmol.g^{-1} and a specific surface area of 18.4 m^{2}.g^{-1}. The resin was washed with water and pretreated overnight with 2 mol. l^{-1} HCl before being slurred to columns for loading. The PGE were measured using a quadrupole ICP-MS (VG, Plasma Quad 2+) using the scanning mode. ^{115}In and ^{187}Re were used as internal standards. Calibration was achieved using freshly prepared solutions in the range of 0.5-5 ng.ml^{-1}. The stability of these solutions was tested over several weeks. It was observed that Pd solutions were unstable in this concentration range, even at 4°C. After two weeks, palladium concentrations decreased during storage and its stability was not improved by the addition of Cl^{-1}. In contrast, Rh and Pt solutions were stable over a two-month storage interval at 4°C.

Analytical procedure

Ashing. All samples were cleared of coarse particles, under microscope without washing, and then dried at room temperature. Prior to analysis, the mosses were dried at 24°C to constant weight (approx. 24 hours). Samples were finely ground using an agate mill. Portions of the sample, about 2 to 10 grams, were transferred to a quartz beaker, subjected to a 2-step burning in an electric oven, carbonated for 3 hours at 220–230 °C, and finally ashed for another 3 hours at 650–670°C.

Digestion. The ash was transferred from the quartz beaker to a PTFE digestion bomb using 10 ml aqua regia ($HCl:HNO_3$ 3:1). Acid digestion lasted 3 hours at 200 °C. After evaporating of the solution to near dryness and adding another 5 ml of 40% HF, the digestion was repeated for another 3 hours at 200 °C. The solution was evaporated again to near dryness and HF was eliminated by adding of 2 ml of concentrated HNO_3 and evaporating to dryness.

Separation. The residue was dissolved in 20 ml of 1.2 mol.L^{-1} HCl, and loaded from the top of the Amberlyst A-26 column (50 mm resin bed). The bomb and the column were rinsed twice using 10 ml of 1.2 mol.L^{-1} HCl at 1 ml.mn^{-1}. The fixation solution and the rinsing solution were discarded. The column was eluted with 20 ml of 2.0% thiourea at a flow rate of 1 ml.mn^{-1}. All flow rates must be well controlled.

Dissolving. The eluate was collected in a 50 ml PTFE beaker and carefully evaporated to near dryness on a hot plate. The residue was dissolved with 5 ml of 6 M HNO_3. The solution volume was slowly decreased by evaporation to about 0.5 ml, then transferred to a 25 ml PE measurement tube. The beaker was washed using 0.2 M HNO_3 and the solution transferred into the tube. The volume of the final solutions was 19.8 ml. Internal standard elements were added in order to obtain a concentration of 10 ng.ml^{-1}. Solutions were kept at 4 °C until analysis. Storage before analysis never exceeded one week.

Table 4.4.2. Concentrations of Pt and Pd in mosses collected near the A6 highway, located 50 km south of Paris in 1999 (µg.kg^{-1} of dry weight).

Moss species (dist. from roadside)	Pt	Pd	Pt/Pd
Cirriphyllum piliferum (5m)	8.1	1.3	6.2
Eurhynchium speciosum (5m)	9.1	0.9	10.1
Physcomitrium eurystomum (5m)	12.0	3.1	3.9
Physcomitrium eurystomum (5m)	12.0	2.3	5.2
Pylasisia polyantha (5m)	5.8	1.8	3.2
Rhacomitrium canescens (5m)	5.2	5.8	0.9
Polytricum formosum (10m)	1.7	<0.5	
Eurhynchium speciosum (10m)	4.4	<0.6	
Scleropodium purum (15m)	2.4	<0.5	

Chemical recoveries were tested for Pt and Pd (additions of 10 to 100 ng of Pt and Pd to 1 g of dry moss) and indicated that the recovery reached 95 %. The detection limit was calculated to 0.06 µg.kg^{-1}, for a 10-g sample weight. The uncertainties were 10 and 20 % for concentration of 1 and 10 µg.kg^{-1} respectively.

Passive biomonitoring

As it can be seen from literature (Djingova et al. 2003; Niemelä et al. 2004), the passive biomonitoring (use of endogenous plants) with mosses is a difficult matter because of the difficulty to find specimens very close to the road. The sampling site selected for this study was a forest, the Fontainebleau forest 50-km south of Paris crossed by the A6-highway (65,000 vehicles/day). A 10-meter long area where mosses were growing was found near to the road edge. Each moss was sampled and analysed separately. The moss species were *Cirriphyllum piliferum, Eurhynchium speciosum, Physcomitrium eurystomum, Pylasisia polyantha, Rhacomitrium canescens*, *Polytricum formosum* and *Scleropodium purum*. The sampling distance to road edge ranged from 5 to 15 meters. Table 4.4.2 gives Pt and Pd concentrations in the 9 mosses.

Pt and Pd concentrations in mosses collected from the roadside were significantly higher than those in the unpolluted mosses, ranging from 5.2 to 12 µg.kg^{-1} of dry matter for Pt and 0.9 to 6 µg.kg^{-1} for Pd. A group of samples was collected at a 5-meter distance from the highway. They display average Pt and Pd concentrations of 8.7 ± 2.7 µg.kg^{-1} and 2.5 ± 1.6 µg.kg^{-1}, respectively. Pt/Pd ratio ranged 0.9 to 10.1, with an average of 4.9 ± 2.8.

For samples from a second group of mosses taken at 10- and 15-m distances, the Pt average concentration was 2.8 $\mu g.kg^{-1} \pm 1.1$, while Pd was not detected (<0.5 $\mu g.kg^{-1}$). Thus, a sharp gradient exists near the vicinity of the road, as generally observed in previous studies (e.g. Niemelä et al. 2004). Two cushions of *Physcomitrium* growing at the same distance from road side were sampled separately. The Pt content was the same for both cushions, but Pd content was different.

Comparing to literature data (Table 4.4.1), Pt concentrations obtained in this present work (Table 4.4.2) are lower, while Pd concentrations are comparable to the published results for mosses. One problem in using natural mosses for passive biomonitoring of heavy metals is that it is generally not possible to know the period when the mosses accumulate elements. This is possibly one of the reasons that may explain the different concentrations of the same element between the various species of mosses collected at the same site. Another reason could be a difference in Pt and Pd solubility in rain (Amosse and Delvos, 2002) or the capture efficiency according to species and element differences. In addition, emission heterogeneity, as shown by the heterogeneous sample-to-sample composition for roadside dust (Farago et al. 1998), may add some variation to the results. The average Pt/Pd ratios reported for roadside dusts are highly variable (Ravindra et al. 2004). In addition, converter technology has changed over time and is not uniform in all the countries where they are used. The PGE concentrations in plants exposed to traffic pollution is the result of a number of parameters. Among them, several parameters can be listed: plant species, traffic intensity, converters technology, wind direction, distance from road, preparation procedure and analytical procedure. At this point, the comparison of data issued from different studies is questionable. Nevertheless, if only one parameter is variable when all the other are maintained constant, the comparison is valuable. It is the case for the retrospective study of one site with the same species (Helmers and Mergel, 1998) or the comparison of different species in the same site (Djingova et al. 2003; Niemelä et al. 2004).

Active biomonitoring

The advantages of active versus passive monitoring are numerous. The species, the distance from road, exposure site and duration can be chosen. The mosses have demonstrated their ability for PGE accumulation. Thus, they were chosen for this active biomonitoring test.

The mosses used for active biomonitoring experiments were sampled in the Fontainebleau forest, which is located 50 km south of Paris. The sampling site was located at a distance more than one kilometre from high traf-

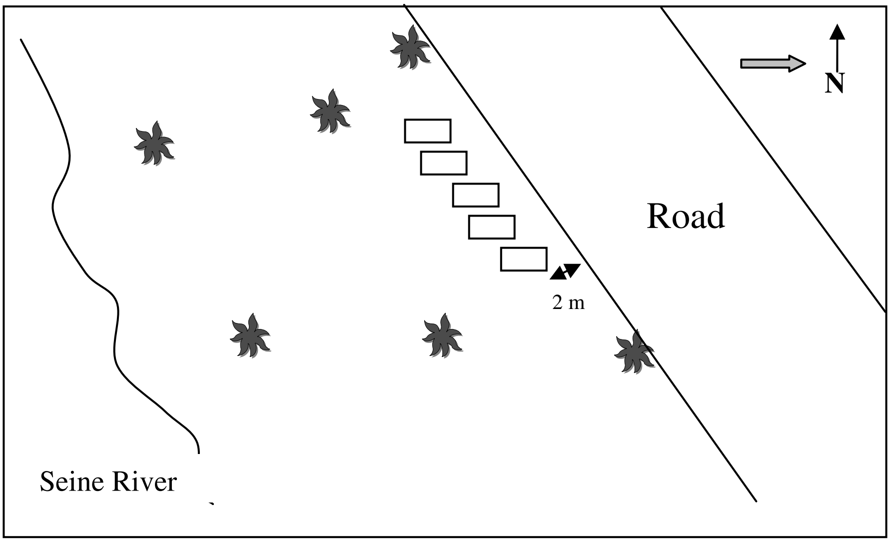

Fig. 4.4.1. The Bois de Boulogne camping is bordered by a road and the Seine River. The trays containing moss cushions were set 2 meters from the road edge, avoiding the small trees and exposed for one month. The gray arrow represents the prevailing wind direction

fic motorways and under a tree canopy. Two samples from this "unpolluted" site, so-called blank mosses, *Scleropodium purum* and *Polytricum formosum,* were analysed. Concentrations of <0.2 $\mu g.kg^{-1}$ and 0.6 $\mu g.kg^{-1}$ were determined for Pt, respectively. Palladium concentrations were below the detection limit (<0.2 $\mu g.kg^{-1}$) for both species. The moss *Polytricum* is most liable to soil contamination because of its morphology. *Scleropodium p.* was then retained for further experiments. Previous work in our laboratory has shown the ability of this species, to be used as a biomonitoring tool for heavy metals deposition (Amblard-Gross et al. 2002).

Scleropodium purum was sampled in this site and the moss cushions were set in plastic trays. The mosses were acclimated to the trays in open air area near the laboratory for two days and then transported to Paris.

The exposing site was the Bois de Boulogne camping in the west of Paris. This site is bordered by a road with very dense traffic on one side, and by the Seine River in the other side (Fig. 4.4.1). This represents the typical urban driving mode (automobiles having speeds from 0 to 70 $km.h^{-1}$ during the night and week ends; 0 to 30 $km.h^{-1}$ during peak-hours of work

Table 4.4.3. Pt and Pd concentration (µg.kg^{-1} dry weight) in *Scleropodium purum*, exposed for one month to an urban area west of Paris

	Pt	Pd	Pt/Pd
	2.4	0.7	3.2
	2.7	1.2	2.3
	1.9	0.8	2.3
	3.8	1.7	2.2
	3.5	0.7	4.8
	4.3	2.5	1.7
Mean	3.1	1.3	2.8
Standard dev.	0.9	0.7	1.1

days in the morning between 7 am and 9 am and the afternoon between 5 and 7 pm). Furthermore, trucks and buses do not use this road which tends to decrease the contribution of diesel motors to roadside pollution when compared to highway traffic. This site allows the exposure of moss transplants in an urban context. It was possible to set the mosses directly on soil in relatively safe conditions. Otherwise, biomonitors settled in busy streets are usually destroyed, even when put on a bus shelter top. Its main disadvantage was to not be to the windward of the prevailing wind direction.

The trays containing the moss cushions were set to 2 m from the road edge. Transplants of *Scleropodium purum* were exposed to this environment during one month on February 1999. Results from 6 sub-sample analyses are given in Table 4.4.3. Pt concentrations ranged from 1.9 to 4.3 µg.kg^{-1}, averaging 3.1 ± 0.9 µg.kg^{-1} of dry moss. Pd concentrations ranged from 0.7 µg.kg^{-1} to 2.5, averaging 1.3 ± 0.7 µg.kg^{-1}. The Pt/Pd ratios range from 1.7 to 4.8, averaging 2.8 ± 1.1. The variability observed was less than that for the passive biomonitoring. This is expected as the use of only one moss species means the bioavailability of Pt and Pd remains constant (provided that the chemical form of the element remains the same). The Pt concentrations measured in these mosses were rather low compared to literature. This could be due to the shortness of the experiment, and to the site characteristics (not under prevailing wind direction).

4.4.4 Conclusion

This experiment revealed the ability of *Scleropodium purum* to be used as an active biomonitor of PGE emissions, and more generally, the ability of mosses to accumulate PGE *via* dust deposition during active biomonitoring experiments. The advantage of active versus passive biomonitoring is to reduce the sample-to-sample variability and to allow an exposure on the best conditions, theoretically. The moss accumulation behaviour against some parameters has to be explored. The temporal variability of the accumulation and the effect of rain on content must be checked before undertaking large scale active biomonitoring for PGE with mosses.

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4.5 Distribution of Palladium, Platinum and Rhodium in Birds of Prey

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Three of the platinum group elements (PGE); palladium (Pd), platinum (Pt), and rhodium (Rh) are emitted in the exhaust gas from automobile catalysts (Moldovan et al. 2002). Resulting increasing environmental concentrations of these PGE have led to a concern over their environmental impact and potential bioaccumulation. A clear link has been established between the increasing use of automobile catalysts and increasing environmental PGE concentrations (Rauch and Hemond 2003; Barbante et al. 2004; Rauch et al. 2004a). However, the extent of PGE contamination in the biosphere, especially the fauna, is poorly documented. The dynamics of these metals in animals at upper trophic levels has recently started to be investigated (Sures et al. 2001; Zimmermann et al. 2002), but to date, there are no studies on the PGE contamination of free-living animals at the top of food chains.

This article presents literature on the area of PGE bioavailability and bioaccumulation, and results from research on PGE distribution in free-living birds of prey.

4.5.1 PGE bioavailability

Automobile catalyst emitted PGE can be transformed into potentially bioavailable species in the environment (Lustig et al. 1998). Uptake has been observed in sediment-dwelling invertebrates in the field (Moldovan et al. 2001), while laboratory studies have shown an uptake of PGE in periphyton communities, mussel, eel and barbel (Sures et al. 2001; Zimmermann et al. 2002; Rauch et al. 2004b). There are indications that Pd has a higher mobility compared to Pt and Rh, possibly resulting in different environmental pathways (Jarvis et al. 2001; Zimmermann et al. 2003). The uptake rate of automobile catalyst PGE in animals was also found to be highest for Pd, followed by Rh and Pt (Moldovan et al. 2001; Sures et al. 2001; Sures et al. 2002).

Investigations on the environmental routes and uptake of PGE in animals at higher trophic levels are still scarce (Ek et al. 2004a). To assess the bioavailability and pathways of PGE, the distribution of PGE in birds of prey and their spatial and temporal trends were investigated (Jensen et al. 2002; Ek et al. 2004b; Ek et al. 2004c).

Birds of prey are exposed to metals *via* internal or external contamination (Goede and de Bruin 1984). Internal contamination results from ingestion of contaminated prey or inhalation of airborne particles while external contamination results from the deposition and attachment of airborne particles onto feathers. Inhaled particles are removed from the lung region by mucociliary clearance and then swallowed, while ultrafine particles reaching the alveolar region are cleared very slowly (Hinds 1999). Metals ingested or inhaled by birds can be stored in tissues or excreted. The kidney and the liver are major metal storage organs as a result of metal binding to metallothioneins (MT), low-molecular weight sulfhydyl-rich proteins (Furness and Greenwood 1993). Binding of Pd to MT has been demonstrated in both *in vitro* and *in vivo* laboratory studies (Nielson et al. 1985; Zhang et al. 1998). Excretion mechanisms are sequestration in feathers or excretion through the digestive tract to the faeces (Burger 1993). Females can also excrete metals in their eggs and eggshells (Burger 1994).

Metal levels in blood reflect the recent dietary intake and mobilization from internal tissues and excretion *via* the digestive tract and sequestration in feathers, eggs or internal tissues (Braune and Gaskin 1987). Metal levels in feathers reflect both the level in blood during the time of feather formation as well as external metal contamination (Goede and de Bruin 1984; Furness et al. 1986).

4.5.2 Bird groups studied

Three bird of prey species, *i.e.* the sparrowhawk (*Accipiter nisus*), the peregrine falcon (*Falco peregrinus*) and the gyrfalcon (*Falco rusticolus*), and two of their prey species, *i.e.* the house sparrow (*Passer domesticus*) and the willow grouse (*Lagopus lagopus*), were studied. The sparrowhawks live in urban or rural areas around the city of Göteborg and their prey, the house sparrow, lives in urban areas in Göteborg. One group of wild peregrine falcon lives in north Sweden, and another group in south Sweden. The wild peregrine falcons live relatively far from urbanisation, at least several hundred metres from major roads. In addition, samples were obtained from captive peregrine falcons living at a breeding station. The gyrfalcon and its main prey, the willow grouse, live in remote areas of north Sweden.

Blood, eggs, faeces and feathers were obtained from the Department of Zoology at Göteborg University. Additionally, part of the feathers used in the time trends were obtained from the Göteborg Natural History Museum, and liver and kidney samples were obtained from the Swedish Museum of Natural History in Stockholm. Sample collection procedures are described in Jensen et al. (2002), Ek et al. (2004b) and Ek et al. (2004c). Feathers were obtained from all bird groups, while the other materials were only from peregrine falcons living in south Sweden because of sample availability. Feathers and dry faeces were stored in polyethylene bags at room temperature. Blown egg contents (both egg white and yolk) were stored in alcohol washed glass bottles at -20ºC. Blood samples were whole blood sampled in ethanol. Kidney and liver samples were obtained from frozen specimens using ceramic knives. Blood, kidney and liver samples were stored in plastic containers at -20ºC.

4.5.3 PGE determination

PGE concentrations in blood, eggs, faeces, feathers, kidney and liver were determined by quadrupole inductively coupled plasma mass spectrometry (ICP-MS) after microwave digestion (Jensen et al. 2002). Spectral interferences were carefully monitored by the simultaneous analysis of interfering elements and by determination of interference formation using solution of interfering elements. Interferences were corrected mathematically (Moldovan et al. 2001; Jensen et al. 2002) and concentrations were removed when the interference was 5 times larger than the actual concentration (Jensen et al. 2002; Ek et al. 2004c).

Suitable CRM do not exist for trace PGE in biological materials and comparisons with other analytical methods were not performed. Three sets of laboratory reference materials (LRM) for eggs and feathers were prepared (Jensen et al. 2002; Ek et al. 2004c). LRM were analyzed together with each batch of egg and feather samples, respectively. The good precision found for PGE concentrations in LRM demonstrates that the results are not affected by random errors and provides confidence in the comparison of results (Jensen et al. 2002; Ek et al. 2004c).

Statistical analyses were performed using the Mann-Whitney U-test for the comparison of bird groups and Spearman rank correlation for the study of temporal trends (Siegel and Castellan 1988). The significance level is expressed as $p<0.05$.

For the investigation of external versus internal PGE contamination of feathers a laser ablation ICP-MS procedure was developed (Jensen et al. 2002; Ek et al. 2004b). The procedure, which involves ablating scan lines across the shaft of feathers, was applied to the analysis of primaries and rectrices from birds from all different groups (Jensen et al. 2002; Ek et al. 2004b).

4.5.4 Spatial and temporal patterns in feathers

Spatial patterns of PGE were investigated by analysing feathers from the different bird groups (Fig. 4.5.1) (Jensen et al. 2002). Feathers of all birds of prey studied were similar in size, growth rate and growth period, and were therefore considered to be comparable. No statistical difference in PGE concentrations was observed and it is therefore assumed that PGE concentrations in feathers of birds of prey reflect the natural background. This is supported by the relatively low concentrations.

In contrast, PGE concentrations in house sparrow feathers were significantly higher than in the other bird species, including the willow grouse (Fig. 4.5.1). House sparrows commonly take dust baths and therefore, the higher concentrations are expected to be the result of both habitat and behavior. As a result, preys in urban areas could be a source of PGE to animals at higher trophic levels.

Temporal patterns were investigated in the feathers of sparrowhawks (living 1939-1996) and peregrine falcons (living 1917-1999) (Fig. 4.5.2). Increasing concentrations were observed for all the PGE, although the trend was only statistically significant for Pd and Rh in peregrine falcon and Rh in sparrowhawk (Fig. 4.5.2) (Jensen et al. 2002). This temporal increase agrees with the theory that the introduction and use of automobile catalysts has led to increased environmental PGE concentrations.

4.5.5 PGE distribution in birds of prey

PGE bioaccumulation was studied by analysing different materials from peregrine falcons living in south Sweden (Fig. 4.5.3). Palladium concentrations were significantly higher in feathers compared to kidney, and Pd concentrations were also significantly higher than Pt concentrations in liver.

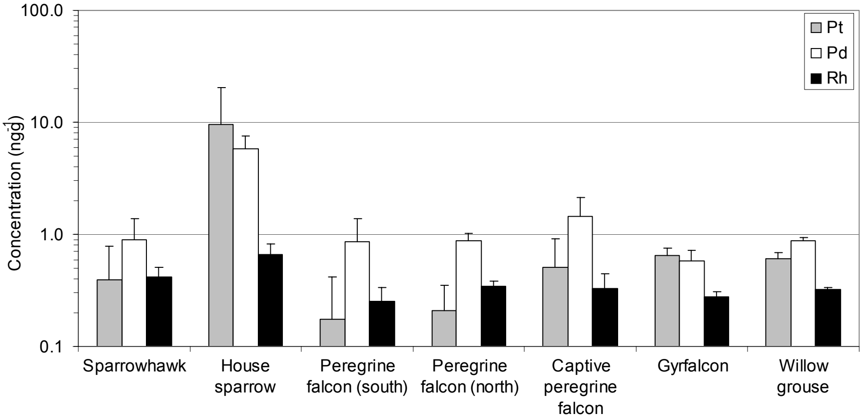

Fig. 4.5.1. Geometric mean PGE concentrations in flight feathers from sparrowhawk, house sparrow, peregrine falcon, gyrfalcon and willow grouse living after 1986. Bars represent standard errors of the mean. Note the logarithmic scale. The number of individuals were: sparrowhawk, 23 (Pd), 35 (Pt, Rh); house sparrow 8 (Pd), 6 (Pt), 2 (Rh); peregrine falcon (south), 8 (Pd, Pt, Rh); peregrine falcon (north), 2 (Pd, Pt, Rh); captive peregrine falcon, 12 (Pd, Pt, Rh); gyrfalcon, 3 (Pd, Pt, Rh); willow grouse, 2 (Pd, Pt, Rh)

Platinum concentrations were significantly higher in blood compared to liver and kidney, and Rh levels were significantly higher in blood and liver compared to feathers (Fig. 4.5.3) (Ek et al. 2004c).

A comparison of PGE concentrations in egg, liver and kidney with concentrations in blood indicates that Pd is more readily transferred to the liver than Pt and Rh. Palladium may also be sequestered into feathers (Jensen et al. 2002; Ek et al. 2004c). It has been shown that Pt and Pd bind strongly to metallothionein (MT) in the liver and kidney of rodents (Zelazowski et al. 1984; Zhang et al. 1998). However, comparison of PGE distribution with the distribution of metals with a known bioaccumulation mechanism, i.e. Cd, Cu and Zn, indicate that binding to MT is not a major bioaccumulation mechanism for PGE, possibly due to relatively low concentrations (Ek et al. 2004b). A comparison with the distribution of Cu, Zn, Cd and Pb in the same materials indicates that PGE uptake and metabolism is different to the latter metals (Ek et al. 2004b). Metals tend to concentrate and be retained in one particular compartment at much higher levels than in others; this was not found for the PGE in birds (Ek et al. 2004b).

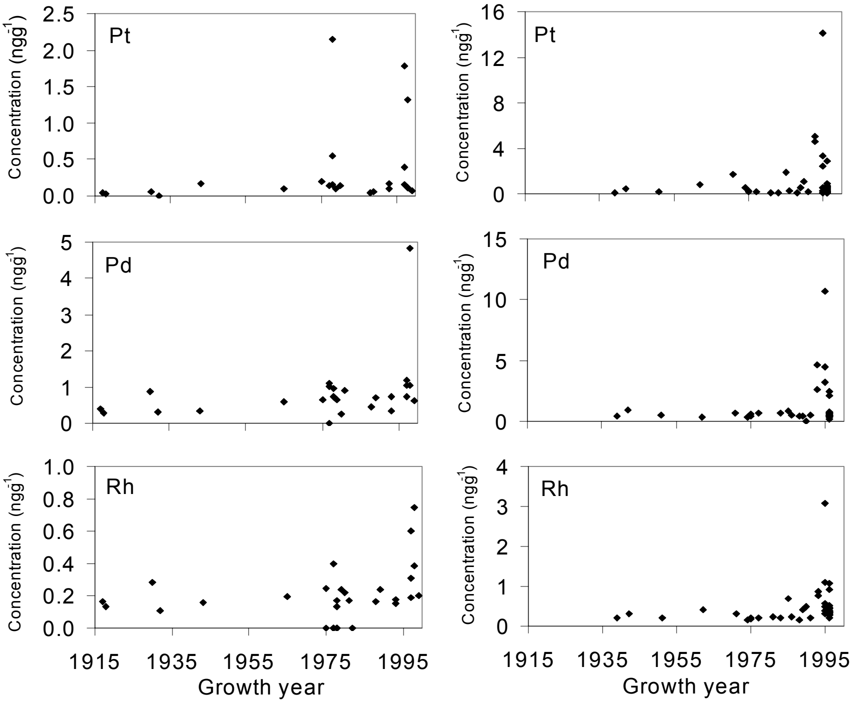

Fig. 4.5.2. PGE concentrations in flight feathers of peregrine falcon, south Sweden (1917-1999) (left) and sparrowhawk (1939-1996) (right). Each point represents one individual bird. Note the different concentration scales. Adapted from (Jensen et al. 2002), reprinted with permission. Copyright 2002, Springer

Laser ablation-ICP-MS analysis suggests an external PGE contamination of feathers, possibly in the form of submicrometer-sized particles attached to the feathers (Jensen et al. 2002; Ek et al. 2004b). Adhesive forces of micrometer-sized particles to surfaces are known to be very strong (Hinds 1999), causing such particles to attach firmly to feathers. PGE occur as abundant randomly distributed sharp peaks in the LA-ICP-MS profile, which indicates the presence of small heterogeneously distributed external PGE particles. Fig. 4.5.4 exemplifies this for one sparrowhawk feather. Approximately 85% of the peaks represent particles of maximum 0.5-1.5 µm in diameter, containing low PGE concentrations. A few larger particles (maximum ~3-7 µm) containing higher PGE concentrations were also detected. In air, PGE were detected in particles with diameters ranging

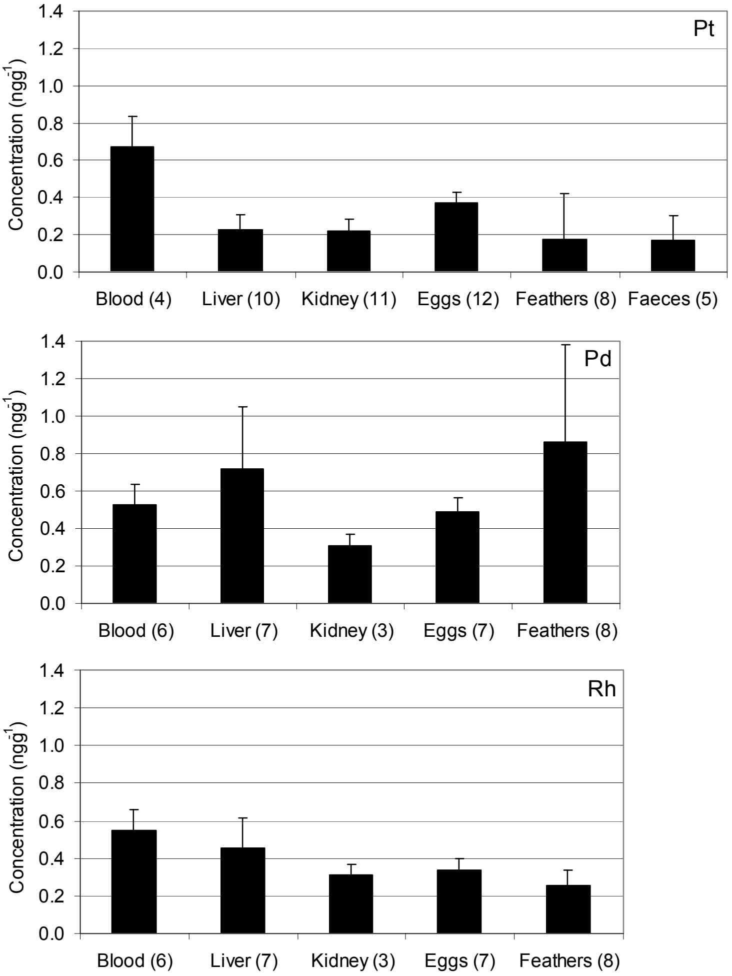

Fig. 4.5.3. Geometric mean of PGE concentrations (dry weight) in blood, eggs, faeces (only Pt), feathers, kidney and liver from peregrine falcon living in south Sweden. Note the different concentration scales for each PGE. Bars represent standard errors of the mean. Number of samples for each material is shown in parenthesis

from <0.39 µm to >10 µm (Palacios et al. 2000; Gómez et al. 2001; Rauch et al., 2001; Gómez et al. 2002; Kanitsar et al., 2003), In addition, 11-36 % of the particles emitted from automobile catalysts were found to be <3.14 µm (Artelt et al. 1999).

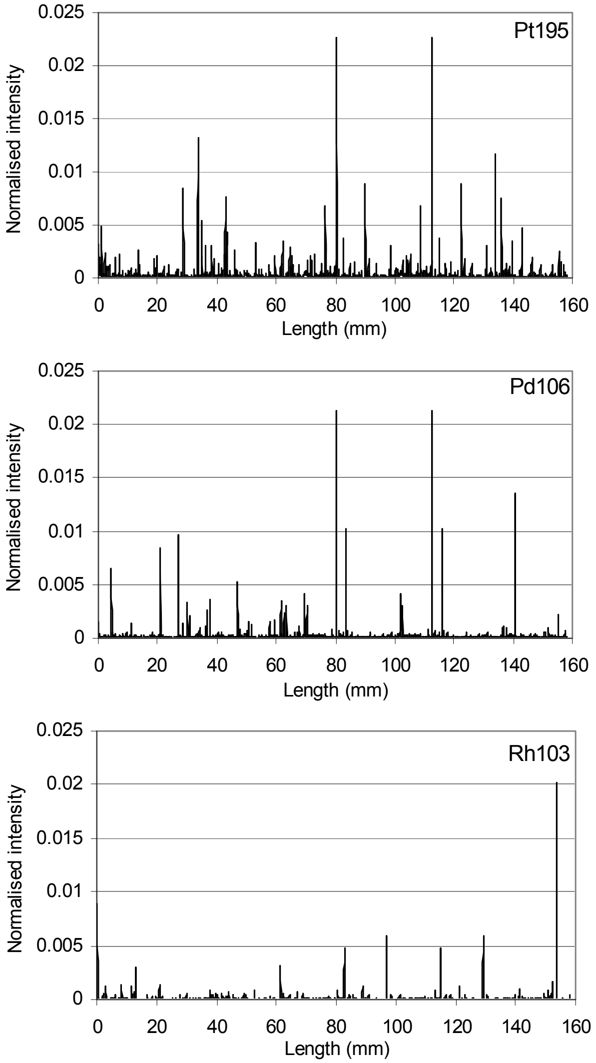

Fig. 4.5.4. Laser ablation ICP-MS profiles for PGE along the feather shaft of a sparrowhawk primary grown in 1996. Metal intensities are corrected for isotopic abundance and normalized against ^{44}Ca intensity. The x-axis is the length of the feather shaft (0 mm = base of shaft). Adapted from (Ek et al. 2004b), reprinted with permission. Copyright 2004, Springer

Internal contamination is reflected in the low baseline of the LA-ICP-MS profiles (Fig. 4.5.4), present for feathers from all bird groups. This low baseline suggests that internal PGE contamination is taking place, but that it is limited compared to external contamination.

4.5.6 Conclusion

The potential for birds of prey to bioaccumulate palladium, platinum and rhodium was investigated. The results presented here show that PGE levels in birds of prey are low despite increasing environmental concentrations. Birds of prey living in urban areas are exposed to PGE-containing airborne particles and there is evidence that fine PGE containing particles stick to feathers, although these particles do not result in a significant PGE concentration increase. Airborne particles may also be inhaled by the birds and elevated PGE concentrations in potential preys may result in the ingestion of PGE. However, PGE bioaccumulation was found to be relatively limited and current PGE concentrations in the environment do not seem to be a risk for birds of prey. Although PGE accumulation via food chains were not found to result in elevated PGE levels in birds of prey, it remains important to monitor changes of PGE in free-living animal species, especially those more directly exposed to automobile exhaust fumes. Particular attention should also be given to Pd owing to its higher mobility and bioaccumulation potential.

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5 Health Risk Potential of Palladium

Although the benefits of using autocatalysts are widely recognized, there is much debate and controversy regarding the potential risks associated with their use in terms of humans and the environment. Platinum emissions from catalytic converters are mainly regarded as posing a low risk to the general population given the current state of knowledge (see "Anthropogenic Platinum-Group Element Emissions – Their Impact on Man and Environment", Zereini & Alt (Eds)). The potential for emitted Pd to elicit toxic responses is, however, viewed more critically given the higher solubility and bioavailability of this metal.

Orion & Wolf (Section 5.1) discuss the topic of contact dermatitis to Pd. They focus on exposure effects in humans, treatment and Pd patch test results. In Section 5.2, Nygren details the various uses of Pd, occupational exposure to these metal and related monitoring methods in the workplace in his contribution "Palladium occupational exposure". Wiseman (Section 5.3) reviews the current knowledge regarding Pd in the environment, exposure levels, toxicity and the human health risk potential of emissions from autocatalysts. According to Wiseman, there is not enough information on the toxicity of Pd to allow for an adequate assessment of risk. The other authors in this chapter share a similar view. Wiseman suggests that more information is needed regarding the mobility, transformation behaviour and bioaccumulation potential of Pd and other PGE in the environment to fully judge their possible impacts. The editors of this book support these conclusions. Melber and Mangelsdorf (Section 5.4) conclude this chapter with an overview of palladium toxicity in animals and in *in vitro* test systems.

Zereini & Alt (Editors)

5.1 Contact Dermatitis to Palladium

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5.1.1 Contact and Dermatitis

Contact dermatitis is the most common pathologic response pattern resulting from skin contact with a chemical agent, natural or synthetic. Although these reactions are extremely common and are frequently encountered in dermatology, the process was not recognized until Jadassohn first described contact allergy to mercury in 1895 [1]. Since then, great developments in the field of contact dermatitis have occurred. We can now distinguish between several pathologic and clinical reactions, understand the mechanisms better, and test for suspected offending materials.

There are two major pathways to develop contact dermatitis: allergic and irritant. Allergic contact dermatitis, mainly in the form of eczema, is simply inflammation of the skin with spongiosis or intercellular edema of the epidermis (the outermost layer of the skin), which evolves in an immunological mechanism. It comprises about 20% of cases of contact dermatitis. Irritant contact dermatitis comprises the other 80% of cases and involves a non-immunological mechanism.

Allergic contact dermatitis is a classic delayed hypersensitivity reaction, also called type IV immunologic reaction, and is mediated by immune cells rather than by antibodies. It is agent-specific and requires prior sensitization; on second encounter with the offending allergen, an elicitation response occurs.

Irritant contact dermatitis happens through direct damage to the skin without prior sensitization, and is thus non-specific. Clinically, it can be quite tricky to distinguish between the two.

Patch testing is a well-established method of diagnosing allergic contact dermatitis. Patients with a history and clinical picture of contact dermatitis are re-exposed to an array of suspected allergens introduced onto the skin in small concentrations under controlled conditions. The preferred sight for testing is the upper back, where several strips of tape, holding small allergen-containing chambers, are placed for about 2 days. Ideally, two readings of results are performed: at the same day of the removal of the patches, and 2-4 days later. Positive results are recorded as +/++/+++, according to the degree of redness and infiltration of the skin.

Although a cardinal tool for diagnosing allergic contact dermatitis, patch test results may vary, and can be influenced by age, sex, atopy, medications and more.

Patch tests are performed using palladium chloride 1% in petroleum.

5.1.2 Human exposure to Palladium

Palladium is a heavy transitional metal whose use has become more and more popular in past decades. It is used in dental appliances, chemical catalysts, electrical appliances and fine jewelry, but the greatest increase in palladium demand has been in automotive exhaust catalytic converters [2]. Even though, according to measurements, human palladium exposure levels through street dust is very low, the general population may come into contact with the metal mainly through mucosal contact with dental fillings or dentures and skin contact with fine jewelry containing palladium. In several countries, palladium has started to displace the traditional amalgam in dental fillings because of concerns about mercury toxicity, and gold due to the price factors [3]. Palladium can be also frequently found as a component of white gold and other jewelry alloy.

The extent to which palladium is released from dental fillings depends on the type of alloy used, but varies between individuals according to the state of their teeth and personal habits [2, 4]. Dental fillings are the most common route of exposure to this metal resulting in skin or mucosal problems. It is estimated that, depending on the palladium content and number of fillings, around 1.5-15 micrograms per person per day are released. Indeed, very small amount of palladium ions are required to cause an allergic reaction in sensitive people [5].

Dealloying has been proposed as a possible corrosion mechanism in high-palladium alloys. Palladium has a high level of galvanic current density when near other metals, with the current density of palladium alloys approximately 10 times higher than for high noble alloys [6]. This enables extensive migration of palladium to saliva, tooth roots, jaws, gums, and other parts of the body (systemic reactions).

5.1.3 Type of reactions to Palladium

Some palladium salts are strong contact irritants and are considered unsafe for contact with the skin, whereas others, such as palladium chloride show minimum irritancy [7]. Workers occupationally exposed to palladium salts come from the chemical industry and may suffer from primary skin and eye irritation. Palladium-containing dental alloys were introduced to the market around 1973, and palladium allergy emerged in the literature soon after [8]. The site of reaction to palladium depends on the exposure source. Recorded allergic reactions include contact stomatitis [9] with eczematous and lichenoid histologic changes, linear lichen planus, a rash involving either skin and/or mucosa [10] accompanied with itching and unusual sensations in the mouth, periodontal gum diseases, dermatitis at the site of contact with the metal [11], like hand dermatitis or body dermatitis [12]. Even sarcoidal-type allergic contact granuloma was recorded [13]. It is hypothesized that allergic reactions to palladium depends on the arrangement of the metal electrons. The sensitization may not be depended on the element itself but on the complexes formed by the different compounds [14].

5.1.4 Patch tests results

Sensitization to palladium is increasing by the year as reflected in contact dermatitis clinics throughout the world. In several western countries, the incidence of palladium sensitization was recently recorded. In Austria, a sensitization rate of 8.3% was found in unselected eczema patients [3]. In Germany, 7.4% had a positive patch test to the metal [15], 9% was the number in mainland Britain [16], 9% in Turkey [17], 2% in Northern Ireland [18] and 13% in Israel [8]. It is interesting to note the two opposite "out of line" results from Northern Ireland and Israel. These results may represent true variations in the frequency of palladium sensitization in those countries, or simply be a reading error of patch test results. In any case, it appears that the average incidence of palladium allergy is around 7-9% in western countries.

A Turkish study found that palladium-chloride positive patch teat results were recorded more frequently among young women less than 40 years [17].

About one third of nickel-positive reactors will react also to palladium chloride [19]. Great confusion can be found in the dermatological literature concerning this finding, and many authors debate whether this represents a true allergy to palladium or maybe it is merely cross-reactivity of the metals. These authors are not convinced that true allergy to palladium exist, and that positive patch test results are relevant to the patients' rash.

Several main explanations try to offer a solution to cases with concomitant positive patch test reactions: 1) it is thought that contamination of patch test material with small amounts of nickel may create an additive effect, so that two allergens at too low concentrations to elicit a reaction cause a reaction greater than either one alone [20]; 2) nickel and palladium are both in the same group in the periodic table of the elements, and share similar chemistry and electron arrangement. It was demonstrated that the concomitant positive reactions of nickel-sensitive patients to palladium should be considered true cross-reactivity at the T-cell clone level [21]. Needless to say, that each explanations has its supporters and opponents.

Positive patch tests reactions to palladium alone, without concomitant reactions to other metals are rare, but exist [8,10, 22-23]. To our understanding, since those rare cases are usually relevant to the patients' symptoms, this is a proof that palladium can cause true allergic reactions, and some cases represent palladium allergy rather than a concomitant reaction to nickel. Also, in some cases the positive patch test reactions to palladium exceed in strength those to nickel [8].

5.1.5 Treatment

In treating any type of contact dermatitis, avoiding contact with the offending agent is the name of the game. It is advised that persons with a known allergy to palladium should not work with this metal. Protection of the public may be achieved by the use of alloys with high corrosion stability and thus minimum release of palladium.

In dental patients who are sensitive to palladium restorations, palladium-containing materials should not be used. The WHO recommends instructing dentists worldwide about the composition of the alloys and the possible effects of palladium sensitization.

Those patients who have a known allergy to nickel should be informed that, although uncommon, a concomitant palladium allergy may develop [2].

Topical or systemic steroids, as well as anti-histamines can be used to treat the rash and pruritus.

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5.2 Palladium Occupational Exposure

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5.2.1 Introduction

This chapter deals with an occupational hygiene perspective of palladium (Pd). Pd exhibits unique properties that have given this element more and more anthropogenic use. Pd will consequently occur in several work environments and may cause undesired and possibly hazardous occupational exposure to many groups of workers.

Pd is a silvery white metal with atomic number 46 and atomic weight 106. Pd belongs to group VIII, the platinum (Pt) group elements (PGE) in the periodic system. The PGE group is divided into two subgroups, "light" and "heavy" elements. Pd belongs to the light PGE subgroup. Pd is relatively inert in its elemental state and is more plastic than Pt. All elements in PGE group including Pd, are widely distributed but still rare in the earth crust (Hägg, 1963).

Of the PGE group elements, primarily Pd, together with Pt and ruthenium (Rh), have gained significant anthropogenic use (Hägg, 1963). There are four major categories of sources for occupational exposure: mining, refining, processing and product use. Pd can therefore be expected to be present in many different work environments. Undesired exposure with negative health effects may, consequently, occur. There is, however, very limited information on methods used for monitoring of occupational exposure to Pd as well as studies to assess such exposure.

5.2.2 Antropogenic use

Palladium

The element Pd is primarily used because of its catalytic properties and chemical resistance. Pd is used alone or more frequently in combination with Pt, in alloys with Pt or in combination with other base metals (Hägg, 1963; Lindell, 1997). Some examples are for production of sulfuric acid (Beliles, 1994; NAS, 1977), for catalytic increase of the petrol octane rate (Beliles, 1994; NAS, 1977) and for exhaust-gas control (NAS, 1977). Pd has, over time, been the cheapest PGE and has therefore been used for budget price Pt-like jewelry (Hägg, 1963). During recent time Pd has more and more become used as replacement of Pt in catalytic converters (Merget et al, 2001). The lower price of Pd and for many applications comparable properties, also makes Pd a useful substitute for Au. Pd alloys with nickel and silver are used in electronic industry. Plating with Pd can be made using several low temperature processes that are suitable for electronic products (Abys, 2000).

Palladium with PGE

Pd is being alloyed with gold (Au) for use in dentistry (Hägg, 1963). Alloys with Pd and Pt and/or Rh is widely used in the oil industry for upgrading petrol octane rate as well as in the chemical industry, e.g., for production of nitric acid (Beliles, 1994; Lindell, 1997; NAS, 1977).

PGE, including Pd, emanating from automotive exhaust catalytic converters, emitted to the environment and causing exposure of the general public have been reported (Merget et al, 2001). There are also reports of possible occupational exposure to PGE salts during production of automotive catalytic converters (Granlund, 1991). Merget et al (2001) and Rosner et al (1998) have also made some risk evaluations of the exposure to Pd, and other PGE, emitted from automotive catalytic converters. Although there are several studies on Pt levels in the general population and on occupational exposure in various work environments, there is still a significant lack of research on the exposure to Pd in the occupational environments.

5.2.3 Monitoring methods for assessment of work environments

Pd occurs in work environments mainly in aerosols and can be sampled using validated aerosol sampling methods for occupational environments (NIOSH, 1996; OSHA, 1991). A pre-weighed membrane-filter, mounted in a sampling cassette and attached on the workers lap or shoulder, is normally used for sampling the aerosol. A battery pump, connected to the sampling cassette and carried at the workers waist, is usually applied for pumping air through the filter with a calibrated flow rate. During sampling, the aerosol is collected on the filter. The filter is weighed after sampling and the weight difference is the amount of aerosol collected.

The analytical methods used for studies of Pd for occupational exposure assessment are primarily based AAS and ICP-AES (Bernhard et al, 1992; Hery et al; 1992; NIOSH, 1996), ICP-MS (Rauch et al, 2000; Schramel et al, 1997), or X-Ray fluorescence (Messerschmidt et al, 2000). AAS, ICP-AES and ICP-MS all require a sample pre-treatment that involves a dissolution step to convert the sample into a solution. Standardised dissolution procedures are described in an International Standard (ISO, 2002). Other, less common, methods that also have been employed for determination of Pd, are neutron activation analysis (NAA) (Nicolaou et al, 1987; Sabbioni et al, 1987; Tomza et al, 1983) and high performance liquid chromatography (HPLC) with UV detection (Philippeit et al, 2001). Although Rh can been determined simultaneous with Pt using adsorptive cathodic stripping voltammetry (ACSV), Pd cannot be analysed by ACSV (León et al, 1997).

5.2.4 Occupational exposure

The anthropogenic use of Pd, as well as the use of Rh, is much smaller than the use of Pt. Consequently, in contrast to the situation for Pt, only a very limited number of studies on Pd determination can be found in the literature. Even scarcer are studies of Pd exposure in the occupational environment and biological control of exposed workers and no explicit studies of airborne Pd level in workplace atmospheres have been found.

Kielhorn et al (2002) reports of workers occupationally exposed to Pd. They include miners, dental technicians and workers in chemical industry. The latter are mainly exposed to Pd salts, several of which may cause primary skin and eye irritations.

Skin exposure

Pd can cause skin contacts dermatitis, which is in direct contrast to Pt. This cannot, however, be extrapolated to the respiratory sensitising potential of Pd and its salts. Immediate-type of sensitisation to Pd only occurred in workers already sensitised to Pt (Merget et al, 2001). There were only limited cross-reactions between both elements. In South Africa sensitising of Pt refinery workers has been investigated (Murdoch et al, 1986). Skin prick test and radioallergosorbent test were made to detect sensitivity to Pd and Rh. Of 306 tested workers, there was no one that showed isolated positive response to Pd or Rh. Among Pt positive workers, a few also showed positive responses for Pd and Rh exposure. An evaluation concerning dermatitis and hoarseness among workers in screener stacker areas was carried out by US National Institute for Occupational Safety and Health (Bernhard et al, 1992). A significant health hazard was discovered, since 20 workers out of 36 had work related dermatitis. Biagini et al (1985) found that there is a significant diversity of the immune response between Pt and Pd salts. Purello-D'Ambrosio et al (2001) have in a review pointed out the allergological characteristics of Pd and other heavy metals. They also reports an increasing problem due to increased use of these elements in various applications.

Biological control

Only a few reports of Pd urinary level in exposed workers have been found. Philippeit et al (2001) analysed spot urine samples from 10 subjects occupationally exposed to Pd. They found levels in the range <10 - 2 538 ng L^{-1}, while unexposed subjects were in the range <10 - 28 ng L^{-1} (n=44). In another study (Messerschmidt et al, 2000), urine samples from workers in a catalyst recycling facility were determined for Pd and Au. The Pd level found was in the range 200 - 1 000 ng L^{-1} (n=7), while five non-exposed subjects were below the detection limit < 2.5 ng L^{-1}. In a third study (Schuster et al, 1999), urine samples from 12 exposed subjects were in the range < 80 - 3 400 ng L^{-1}. Urinary Pd levels have also been determined in samples from dental technicians and road construction workers. The result showed significantly higher Pd values in the dental technicians as compared to a control group of urban residents. The road construction workers, on the other hand, only showed a tendency to have higher Pd values as compared to the control group (Begerow et al, 1999).

5.2.5 Conclusions

The lack of reports regarding occupational exposure to Pd clearly demonstrates a need for further research. The increasing use of Pd in automotive catalytic converters will, continuously, increase the emission of Pd, which, consequently, will increase the number of occupational exposed groups. Another motive for additional research is the significantly different health effects of Pd compared to other PGE, i.e. that elemental Pd can cause contact dermatitis.

New methods to monitor skin exposure are being developed (Soutar et al, 2000; Cordis, 1999). In combination with analytical methods suitable for determination of Pd in thin samples (Jenkins, 1999; Nygren, 2002), these methods could be further developed to become valuable tools for assessment of occupational skin exposure to Pd. Methods for speciation would also be valuable tools for assessment of different exposure routes and exposure to various Pd compounds with different health effects.

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5.3 Palladium from Catalytic Converters: Exposure Levels and Human Risk

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5.3.1 Introduction

Since their introduction in North America in 1976 and in Europe in the 1980s, catalytic converters have helped drastically reduce automotive pollutant emissions. This has been achieved using platinum group elements (PGE), which catalyse the oxidation of carbon monoxide (CO) to carbon dioxide (CO_2) and hydrocarbons (HC) to water and the reduction of nitrous oxides (NO_x) to nitrogen (N). At the same time, their use has led to significantly increased levels of PGE in the environment (e.g. Zereini et al. 2001a; Palacios et al. 2000; Moldovan et al. 2002; Zereini et al. 2005). In Germany, platinum (Pt) and rhodium (Rh) concentrations in airborne particulate matter have increased 46- and 27-fold from 1988 to 1998, respectively (Zereini et al. 2001a). Elevated PGE concentrations have even been measured in recent snow from central Greenland (Barbante et al. 2001), which indicates that these metals can be transported over long distances.

Previous studies have focused on the environmental contamination of Pt, as this metal dominated PGE emissions in the past. Environmental concentrations of palladium (Pd) have been on the rise though, as it is increasingly used in place of Pt in catalytic converters. Compared to Pt, Pd appears to have a greater solubility and mobility in the environment and is more readily taken up by plants and animals (e.g. Jarvis et al. 2001; Moldovan et al. 2001; Sures et al. 2002; Ek et al. 2004a; Ek et al. 2004b). Unfortunately, less information is available on the environmental concentrations, fate and potential effects of exposure to this metal. This chapter will review the current knowledge regarding Pd in the environment, as well as the possible health effects of its exposure.

5.3.2 Environmental Concentrations and Exposure Levels

PGE have been found in all compartments of the environment. A number of studies have demonstrated elevated levels in airborne particulate matter (Petrucci et al. 2000; Zereini et al. 2001a; Gómez 2002; Zereini et al. 2005), soils (Zereini et al. 1997; Whiteley and Murray 2003), in street dust samples (Jarvis et al. 2001; Zereini et al. 2001b; Gómez et al. 2002; Leśniewska et al. 2004; Whiteley and Murray 2003; Petrucci et al. 2000) and in run-off sediments (Zereini et al. 1997; Zereini and Golwer 1999). PGE have also been found in vegetation (Leśniewska et al. 2004) and organisms such as the freshwater invertebrate *Asellus aquaticus* (Moldovan et al. 2001) and raptors (Ek et al. 2004b).

The inhalation of airborne particulate matter is the primary route of environmental exposure to Pd (World Health Organisation 2002) and is, therefore, the focus of this chapter. Exposure levels to environmental concentrations of this metal via other routes such as through the consumption of food and drinking water are minimal. There are only a handful of studies which have investigated atmospheric levels of Pd (see Table 5.3.1). An early study of air samples collected in the city Chernivtsi (Ukraine) from October to November, 1990 reported Pd concentrations of 56.6 ng m^{-3} (Scheff et al. 1997). This is considerable given that most cars in the Ukraine would not have been equipped with catalytic converters at the time of sampling. A mean concentration of 12.7 ng m^{-3} was reported for Chicago (US) in the same study (Scheff et al. 1997). Kanitsar et al. (2003) measured Pd concentrations of 14.4 and 2.6 pg m^{-3} for particles having a diameter of <30 µm and <10 µm in urban air samples from Vienna (Austria), respectively. They found that Pd was mainly associated with the coarse fraction of aerosols (10-30 µm). Tilch et al. (2000) reported Pd concentrations of 0.2 to 14.6 pg/m^3 in air samples collected in Berlin in 1997. In a study of airborne particulate samples collected in Rome (Italy), comparatively high levels of Pd were measured, with values ranging from 21.2 to 85.7 pg m^{-3} (Petrucci et al. 2000). These levels are comparable to the results of a study of airborne dust samples collected in Rome (Italy) between 1999 and 2000 (Gómez et al. 2002). For downtown and ring-road samples, Pd levels were reported to be 47.2 and 54.9 pg m^{-3}, respectively. Airborne dust from Göteborg (Sweden) was found to contain less Pd, with 4.6 pg m^{-3} for downtown and 1.6 pg m^{-3} for ring-road samples.

Zereini et al. (2005) investigated the heavy metal concentrations in urban air collected at three different locations in Frankfurt am Main (Germany) between August 2001 and July 2002. The particle size distribution of the heavy metals was also determined. For the location with a large volume of traffic, they reported an average Pd concentration of 15 pg m^{-3}. A maximum of 44 pg Pd m^{-3} was measured for this site. The highest concentrations of Pd were found to be associated with particulate matter with an aerodynamic equivalent diameter of 1.1 to 4.7 µm, a particle size which can enter the alveolar region of the human lung.

Table 5.3.1. Pd Concentrations in Airborne Particulate Matter

City	Sample Type/ Location	Sampling Year	Pd Concentrations (pg m^{-3})	Reference
Chernivtsi (Ukraine)	--	1990	56 600 (mean)	Scheff et al. (1997)
Chigaco (US)	--	1990	12 700 (mean)	
Berlin (Germany)	Urban air	1997	0.2–14.6	Tilch et al. (2000)
Rome (Italy)	Heavy traffic	1998-1999	21.2-85.7	Petrucci et al. (2000)
Göteburg (Sweden)	Downtown Ring-road	1999-2000 1999-2000	4.6 1.6	Gómez et al. (2002)
Rome (Italy)	Downtown Ring-road	1999-2000 1999-2000	47.2 54.9	
Frankfurt am Main (Germany)	Heavy traffic Side street Rural area	2001-2002 2001-2002 2001-2002	15.0 (mean) 6.0 (mean) 3.0 (mean)	Zereini et al. (2005)
Vienna (Austria)	Heavy traffic	2002	14.4 (mean) (<30 μm fraction)	Kanitsar et al. (2003)
		2002	2.6 (mean) (<10 μm fraction)	

The results of the Zereini et al. (2005) study confirm the World Health Organisation's (2002) conclusion that ambient air levels of Pd can be expected to be below 0.100 ng m^{-3} in urban areas where Pd catalysts are used. This correlates with an uptake of 2.2 ng per person via inhalation on a daily basis (assuming an average inhaled air volume of 22 m^3 day^{-1}). For comparison, a daily intake of about 1 ng per person is estimated using the highest value of 0.044 ng m^{-3} from the Zereini et al. (2005) study for airborne dust samples from a street with a high traffic load (average inhaled volume of 22 m^3 day^{-1}). For their worst case exposure scenario, Kanitsar et al. (2003) estimated an intake of only 0.16 ng day^{-1}. They, however, only assumed an average inhaled air volume of about 11 m^3 day^{-1}, a rather low rate for an adult. In conclusion, Pd exposure via inhalation can be expected to be less than the World Health Organisation's (2002) calculated uptake rate of 2.2 ng day^{-1}.

5.3.3 Transformation, Mobility and Bioavailability

PGE appears to be emitted primarily in metallic form. Small amounts may also be emitted in an oxidised form. In the case of Pt, for instance, emissions of small amounts of oxidized Pt (IV) have been measured (Schlögl et al. 1987). The evidence suggests that Pd may be rapidly transformed into a more reactive species in the environment and has a greater solubility and bioavailability compared to Pt (Schäfer et al. 1998; Moldovan et al. 2001).

Recent evidence suggests that Pd is more soluble than other PGE and may undergo rapid transformation in the environment. Jarvis et al. (2001) found that 35% of the total Pd in road dust dissolved in a solution at pH 3, similar to rain. This was much higher than that for Rh (1.2%) and Pt (0.5%). About 6% of Pd was found to be soluble in deionised water. Palladium was also found to have a higher solubility rate compared to Pt and Rh. They suggested that Pd is rapidly transformed from a metallic to a chloride species in the environment and is, thus, highly mobile. In contrast, Zereini et al. (1997) conducted solubility experiments on milled samples of a used catalytic converter (monolith) and found that Pt and Rh had only a limited solubility. The highest solubility in rain water was reached at a pH of 1, with 0.35-0.5% for Pt and 1.0% for Rh. Artelt et al. (1999) reported a soluble Pt fraction (in 0.1 molar HCL) of about 1% in their engine test-bench studies. Halogen complexes are likely to comprise the primary fraction of the soluble fraction of exhaust emissions, given the high level of halogens present on the catalyst due to fuel additives (Moldovan et al. 2002). Due to its greater solubility, Pd is likely to be more mobile in the environment than Pt and Rh. There are no data to suggest that Pd can undergo methylation reactions in the environment (World Health Organisation 2002).

Studies of Pt/Pd ratios in environmental and biological media also indicate that Pd has a greater mobility and bioavailability compared to Pt. Zereini et al. (2001b) determined an average Pt/Pd ratio of 18.5:1 in soil, street dust, mud and sediment samples. This ratio is considerably higher than that used in catalytic converters (i.e. about 5:1). In a review of Pt/Pd concentration ratios in environmental and biological materials, Ek et al. (2004a) suggested that Pd is likely to be quickly transformed in the environment and may be more readily taken up by organisms. Specifically, they found that ratios tend to decrease as one goes up the food chain. In environmental media, the Pt/Pd ratio is about 3, while this decreases to about 0.5 in invertebrates and birds. The ratio reaches a low of 0.1 or less in human urine and blood.

Plants and animals have been demonstrated to bioaccumulate PGE, especially Pd. Plants (*Spinacia oleracea*, *Lepidium sativum, Urtica dioica* and *Phacelia tanacetifolia*) grown on PGE contaminated soils have been shown to take up Pd more readily than Pt and Rh (Schäfer et al. 1998). The freshwater isopod *Asellus aquaticus* has also been shown to accumulate greater amounts of Pd compared to Pt, despite greater environmental concentrations for the latter metal (Moldovan et al. 2001). This was further demonstrated in lab experiments involving exposure of *Asellus aquaticus* to PGE standard solutions for a 24 h period (Moldovan et al. 2001). Bioaccumulation factors of 150, 85 and 7 were calculated for Pd, Pt and Rh, respectively. Palladium uptake rates were also shown to be higher in Zebra mussels (*Dreissena polymorpha*) maintained in water containing road dust collected from a highly frequented road in Karlsruhe (Germany) (Sures et al. 2002). Eels exposed to road dust in water (10 kg/100 l) for a 4 week period also accumulated Pd (Sures et al. 2001). Higher concentrations of Pd and Rh compared to Pt have been found in the liver and kidneys of raptors, indicating an uptake of these metals on the order of Pd > Rh >> Pt (Ek et al. 2004b). Liver and kidney concentrations did not indicate bioaccumulation through binding to metallothionein.

Palladium also appears to be more readily taken up by humans compared to Pt. For instance, Pd concentrations were 50 times higher than Pt levels in the blood of unexposed individuals (50.2 and 0.9 ng l^{-1}, respectively) (Begerow et al. 1997). In another study, Pd levels in blood samples from unexposed persons were also found to be considerably higher than Pt concentrations (48 and 5 ng l^{-1} for Pd and Pt, respectively) (Rodushkin et al. 1999). In a study of school children in Rome (Italy), mean concentrations of 7.5 and 0.9 ng g^{-1} Pd and Pt were found in urine (in ng g^{-1} creatinine), respectively (Caroli et al. 2001). Urinary Pd and Rh levels were found to be strongly related to traffic density in the area of residence.

5.3.4 Palladium Toxicity

Information regarding the toxicity of Pd is sparse. Rats given an oral dose of 50 mg Pd powder per kg body weight for 6 months demonstrated delayed rates of weight gain, hepato- and nephrotoxic effects, as well as changes in the mucosal lining of the gastrointestinal tract (Roshchin et al. 1984). Intraperitoneal doses of 14, 28 and 56 µmol palladium (II) nitrate per kg body weight have been shown to inhibit DNA synthesis in the liver, spleen, kidney and testis in male Sprague-Dawley rats (Fisher et al. 1975). The *in vitro* cytotoxic effects of various Pd compounds, and their ability to inhibit enzyme activity, have been well demonstrated (see World Health Organisation (2002) for an overview). The potential of Pd ions to disrupt a variety of processes at the cellular level is attributed to their capacity to form strong complexes with organic and inorganic ligands. There is little evidence for *in vitro* cytoxicity of metallic Pd. Unlike Pt and Rh complexes, Pd does not appear to be genotoxic in mammalian and bacterial cells (Bünger et al. 1996; Gebel et al. 1997). Information regarding the reproductive and developmental toxicity of Pd is lacking. One earlier study demonstrated that Pd in drinking water (5 mg $PdCl_2$ l^{-1}) consumed over a lifetime had a carcinogenic effect in mice (Schroeder and Mitchener 1971). Given the problems associated with this study though, the results must be interpreted with caution (e.g. tumors for males and females were pooled, only a single dose applied, greater longevity for treated males).

The sensitization potential of Pd seems to be the most relevant toxic endpoint for consideration in the assessment of environmental exposure to this metal. Reports of sensitization to Pd have been increasing in recent years, as indicated by patch testing results in various clinics. As many as 13% of tested individuals have been found to react to Pd in such tests (Orion et al. 2003). In one large study conducted by Kränke et al. (1995) with over 10,000 individuals, Pd was demonstrated to be one of the most potent sensitizers among the metals.

5.3.5 Palladium and the Health Risks of Exposure

In sum, Pd appears to be emitted primarily in metallic form, which is considered to be biologically inert. The evidence indicates, however, that a significant fraction of Pd may be rapidly oxidised and solubilized in the environment. Palladium appears to be more soluble and mobile than Pt and Rh. Studies have also shown greater uptake rates for Pd compared to the other PGE. Given these factors, Pd is a cause of concern. However, there is not enough information on the toxicity of Pd to allow for an adequate assessment of risk.

Guidelines in terms of exposure levels to Pd have yet to be established on a national or international level. In their comprehensive review of Pd, the World Health Organisation (2002) avoided making recommendations regarding exposure guidelines, due to the lack of adequate toxicity data on this metal.

Of the PGE, only one study has suggested a rough guideline level in terms of exposure to Pt via inhalation and its potential to elicit an allergic response (Merget and Rosner 2001). From a study of workers in a catalytic converter production plant, Merget and Rosner (2001) recommended a guideline level of 15 to 150 ng m^{-3}. Although they belong to the same group of elements, the applicability of this guideline level in terms of Pd exposure is not suitable. As discussed, some studies have estimated a larger soluble fraction for PGE, especially Pd. Further, uptake rates in organisms appear to be higher for Pd compared to Pt. Palladium appears, however, to be less toxic than Pt. As discussed before, exposure to environmental concentrations of Pd is likely to be low (less than 2.2 ng day^{-1}). The skin sensitization potential of Pd through other exposure routes such as jewellery and dental alloys is considered to be greater than its potential for respiratory sensitization (Kielhorn et al. 2002).

However, environmental concentrations of PGE have increased at an alarming rate in recent years. This warrants the continued monitoring of their levels in environmental media. More information is also needed on the mobility and transformation of Pd and other PGE in the environment and their bioaccumulation potential to fully judge their possible impacts.

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5.4 Palladium Toxicity in Animals and in *in vitro* Test Systems – An Overview

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5.4.1 Introduction

Palladium (Pd) discovered in 1803 by W. Wollaston did not find great interest from toxicologists for a long time, because it belongs to the group of noble metals believed to be of minor toxicological relevance. For over hundred years, Pd had been produced in limited quantities from various sources, mainly from ores in Russia. When the great stores of South Africa (1924) and of Canada (1930) were found, Pd became more widely available. Since the 1970s, demand for Pd from various applications increased remarkably. The world-wide demand of Pd was estimated to yield nearly 300 tons in 1999, with a peak contribution from its use in catalytic converters for automotive emission control (McDonald & Hunt, 1982; Johnson Matthey, 2001).

Parallel to the extended and diverse uses of Pd, the possibilities for exposure via all routes (inhalation, dermal, oral) increased both for the general and the occupational population and led to a growing interest on the toxicological profile of Pd, which can exist in three states: Pd^0(metallic), Pd^{2+}, Pd^{4+}.

One of the first case reports suspecting Pd as a noxious agent has been published in the 1950s and refers to a woman suffering from contact dermatitis by a ring (Sheard, 1955). Since then there was a growing number of reports on adverse health effects in humans due to occupational, iatrogenic (e.g. from use of dental appliances) or other exposures to Pd species. These experiences stimulated also research activities with laboratory animals, whose first sporadic beginnings were in the early 20th century. An overview on the experimental results from laboratory mammals and *in vitro* test systems is given in the following chapter, using the EHC monograph on palladium (WHO, 2002) as a basis.

5.4.2 Palladium toxicity profile

Little is known on the effects of finely dispersed Pd or PdO particles on animals or humans. Some more information is available on tissue reactions after exposure to Pd metal. The majority of studies refers to experiments with Pd ions administered as (soluble) simple or complex compounds, most frequently with $PdCl_2$.

As generally assumed for inhalation exposure to particles (e.g. Hext, 1994; Lechner & Mauderley, 1994; Oberdörster, 1994) , also after inhalation of Pd dust, particle-induced reactions may occur, followed by cellular changes resulting in several diseases. For other routes of exposure, generally it is hypothesized that the effects of Pd metal are mediated via the presence or release of Pd ions. Therefore, animal experiments with ionic Pd are of broad interest for risk assessment of Pd in its different forms and valencies.

Bioavailability and fate in the body

Only few data are available on the kinetics of metallic or ionic palladium. Generally, the absorption of metals and metallic compounds is governed by their solubility in aqueous media.

Elemental palladium

Interestingly, finely dispersed Pd, which is nearly insoluble in distilled water, was found to dissolve appreciably under physiological conditions (blood, gastric juice, biogenic compounds), thus becoming bioavailable to some extent (WHO, 2002). For example, aqueous solutions of amino acids or peptides increased the solubility of Pd dust by a factor of 100 as compared to pure water (Freiesleben et al., 1993). Moreover, the presence of certain complexing agents (EDTA, humic substances, bile) increased the lipid solubility of Pd (Zimmermann et al., 2003).

Uptake and retention of Pd particles in the respiratory tract has been shown in rats. Six months after a single intratracheal application of Pd dust (50 mg/rat; 3.92 µm MMAD), Pd particles have been found to be localized intracellularly in alveolar macrophages (Aughtun et al., 1991).

Pd can also be released from dental alloys. The release is influenced by multiple factors (presence of other metals, processing, surrounding milieu, etc.) and is estimated to be the most relevant source of constant Pd exposure of the general population. Quantitative kinetic data are not available. Skin contact with jewellery, etc. containing Pd may also lead to some bioavailable Pd species, but also here quantitative kinetic data are missing.

Palladium compounds (PdO and ionic Pd)

Pd ions (2+, 4+) can form a variety of simple and complex salts as well as organometallic compounds, some of which are soluble and therefore taken for toxicity testing. Furthermore, such kind of Pd species may be occurring in the human food supply or drinking water.

$PdCl_2$ was poorly absorbed from the digestive tract (< 0.5 % of the initial oral dose in adult rats or about 5 % in suckling rats after 3 - 4 days). Absorption/retention in adult rats was higher following intratracheal or intravenous exposure (Moore et al., 1974, 1975). Absorption after subcutaneous or topical application of Pd compounds was observed (detectable concentrations of Pd in the urine of guinea pigs and rabbits) but not quantified (Kolpakov et al., 1980; Roshchin et al., 1984).

Absorbed Pd has been found in almost all organs, tissues or body fluids of experimental animals (WHO, 2002). After intravenous administration of different Pd compounds, the highest concentrations were found in kidney, liver, spleen, lymph nodes, adrenal, lung, and bone of rats, rabbits, or dogs (Orestano, 1933; Durbin et al., 1957; Fawwaz et al., 1971; Moore et al., 1974, 1975; Ando & Ando, 1994). For example, 21 % of the administered dose of $PdCl_2$ (Ando & Ando (1994) or $Na_2[PdCl_4]$ (Durbin (1960) have been found in liver or kidney of rats 1 day after dosing. After a 4-week dietary administration of the water-insoluble PdO, measurable amounts have been found only in the kidney of rats (Holbrook, 1977).

Urinary excretion rates of intravenously dosed rats and rabbits ranged from 6.4 to 76 % of the administered dose during 3 hours to seven days (Durbin, 1960; Ando & Ando, 1994). Elimination of Pd into faeces ranged in these studies from traces to 13% of administered dose. Following oral administration of $PdCl_2$, > 95% of Pd was eliminated into faeces of rats due to non-absorption (Moore et al., 1974, 1975).

Half-lives calculated for elimination of Pd from rats (whole body, liver, kidney) ranged from 5 to 12 days (Estler, 1992). 104 days after intravenous treatment Pd was still detectable in spleen, kidney, liver, lung and bone (Moore et al., 1974, 1975).

Transfer of small amounts of Pd to offspring via placenta and milk was seen with single intravenous doses of $PdCl_2$ in rats (Moore et al., 1974, 1975).

Owing to the ability of Pd ions to form cemplexes, they bind to amino acids (e.g. L-cysteine, L-cystine, L-methionine; Akerfeldt & Lövgren, 1964), proteins (e.g. casein; silk fibroin; many enzymes; Herblin & Ritt, 1964; Spikes & Hodgson, 1969; Nielson et al., 1985), DNA (see below, section 5.4.2) and other macromolecules, e.g. vitamin B_6 (Pneumatikakis et al., 1989).

Acute, subacute and subchronic toxicity

Pd dust

There are only few studies available investigating the effects of Pd dust. Histopathological changes in the gastrointestinal tract, liver and kidney developed in rats after an unspecified single enteral dose of Pd dust (Roshchin et al., 1984). Daily oral administration of Pd dust (50 mg/kg body weight) over six months resulted in delayed body weight gain and changes of clinical blood serum and urine parameters of rats (Roshchin et al., 1984). Six months after a single intratracheal application of Pd dust (143 mg/kg body weight; 3.92 μm MMAD) several histopathological signs of inflammation have been observed in the lungs of rats (Aughtun et al., 1991).

Pd alloys

Acute and short-term toxicity tests with different Pd-containing dental alloys have been performed with rats. Pulverized oral doses (in gelatine capsules) of up to 1000 mg/kg body weight did not cause deaths or apparent toxic signs, but did cause histopathological changes in internal organs such as lung, liver, kidney, small intestine, and colon. Strong effects were seen with alloy compositions containing copper and/or indium (e.g. Pd/Cu/In; Pd/Sn/Cu; Au/Pd/In). (Culliton et al., 1981; Fuhrmann, 1992; Reuling, 1992; Reuling et al., 1992). The contribution of Pd to these effects is not clear (WHO, 2002).

This is also true for histocompatibility tests with several implants of Pd-containing dental alloys of different compositions. Four to 12 weeks after subcutaneous implantation of the experimental alloys into guinea pigs, mice or rats or after intramuscular implantation into rabbits, the tissue reactions at the implantation site varied from slight to severe. Again, the most extreme reactions were recorded when copper and/or indium were present as additional components (Niemi & Hensten-Pettersen, 1985; Eisenring et al., 1986; Bessing & Kallus, 1987; Reuling, 1992; Kansu & Aydin, 1996).

Pd compounds

Acute toxicity

Pd compounds have a very low to moderate acute toxicity. LD_{50} values in rodents and rabbits ranged, depending on compound and route tested, from 3 to > 4900 mg/kg body weight, the most toxic compound being $PdCl_2$ (which is soluble in water), the least toxic PdO (which is unsoluble in water) (Ridgway & Karnofsky, 1952; Holbrook et al., 1975; Moore et al., 1975; Jones et al., 1979; Williams et al., 1982; Philepeit et al., 1989; Johnson Matthey, 1994a, 1995a, 1997a). Consistent with the low absorption from the digestive tract, oral administration caused the lowest toxicity. For example, $PdCl_2$ showed in Charles-River CD1 rats LD_{50} values of 200 mg/kg for the oral, 70 mg/kg for the intraperitoneal, 6 mg/kg for the intratracheal and 5 mg/kg for the intravenous route (Moore et al., 1975). There were very similar intravenous LD_{50} values of 3 to 7 mg/kg body weight for $PdCl_2$, K_2PdCl_4, and $(NH_4)_2PdCl_4$ (Moore et al., 1975).

Signs of acute toxicity of several Pd salts in rats or rabbits included deaths, decrease in feed and water uptake, emaciation, cases of ataxia and tiptoe gait, clonic and tonic convulsions, cardiovascular effects, peritonitis, hardened gastric mucosa, kidney damage, haemorrhages of lungs and small intestine or biochemical changes (e.g: changes in activity of hepatic enzymes, changes in blood parameters indicative of proteinuria or ketonuria) (Orestano, 1933; Meek et al., 1943; Holbrook et al., 1975; Moore et al., 1975; Wiester, 1975; Roshchin et al., 1984; Philepeit et al., 1989; Johnson Matthey, 1994a, 1995a). Details on compounds and routes tested are tabulated in WHO (2002). Kidney damage has also been confirmed in a recent study. A single ip injection of 20.4 mg/kg body weight of a Pd(II)-dithiocarbamate complex – $[Pd(ESDT)Cl]_n$ – exerted severe and diffuse nephrotoxicity in male Wistar rats. Histopathological findings 48 h after treatment showed widespread acute tubular necrosis involving outer and inner medulla and the subcapsular cortex (Trevisan et al., 2002).

Repeated dose toxicity

The database for repeated dose toxicity of Pd compounds is limited. The only study according to current guide-lines (Johnson Matthey, 1997b) is not published and did not provide a NOAEL (no observed adverse effect level). Nevertheless, an approximate trend of toxicity can be seen from the available studies, whose main results are presented here; a more detailed review is given in WHO (2002).

Effects in rodents and rabbits after short-term (repeated), non-inhalative exposure to various Pd compounds occurred at concentrations in the mg/kg body weight range and referred mainly to changes in biochemical parameters (decrease in activity of hepatic microsomal protein, increase in hexobarbital-induced sleeping time, as an indicator of activation of cytochrom P450) (Holbrook et al., 1976). Clinical signs were sluggishness, weight loss, haematoma or exudations (Kolpakov et al., 1980). Changes in absolute and relative organ weights and anaemia also occurred. One compound (Na_2PdCl_4-egg albumin) caused deaths in mice (Taubler, 1977). Histopathological effects have been observed in liver, kidney, spleen or gastric mucosa of rats (Sprague-Dawley Crl:CD BR strain) 28 days after daily oral administration (by gavage) of 15 and 150 mg $[Pd(NH_3)_4](HCO_3))_2$/kg body weight. Additionally, an increase in absolute brain and ovary weights at the 1.5 and 15 mg/kg dose has been found (Johnson Matthey, 1997b).

Inhalative exposure of rats to chloropalladosamine ($PdCl_2(NH_3)_2$) for about half a year caused slight, reversible (at 5.4 mg/m^3) or significant permanent (at 18 mg/m^3) changes in several blood serum and urine parameters indicating damage mainly to liver and kidney; additionally sluggishness, reduced body weight gain and changes in organ weights were noted, with first changes beginning after 2 weeks. Histopathological information was not given (Panova & Veselov, 1978). Adverse effects including reduction in body weight, changes in several blood parameters and kidney damage (e.g. glomerulonephritis) were also reported with enteral exposure of rats to this salt for about six months. The NOAEL (no observed adverse effect level) was given as 0.08 mg/kg body weight/day (Roshchin et al., 1984.).

Adverse effects on the kidney could be shown also by applying an *in situ* rat kidney perfusion technique. $PdCl_2$-2,6-diaminopyridine·H_2O was able to disturb some functions of the major membrane pumps and proteins (Bikhazi et al. (1995).

Skin, eye and respiratory irritation; sensitization and immunotoxicity

Skin irritation

Skin tests of a series of Pd compounds in rabbits showed dermal reactions of different severity (Campbell et al., 1975; Kolpakov et al., 1980; Johnson Matthey, 1994b, 1995b). A comparative study found the following ranking order: $(NH_4)_2PdCl_6$ > $(NH_4)_2PdCl_4$ > $(C_3H_5\ PdCl)_2$ > $K_2[PdCl_6]$ > K_2PdCl_4 >$PdCl_2$ > $Pd(NH_3)_2Cl_2$ > PdO. The first three compounds caused erythema, edema or eschar in intact and abraded skin, the next three substances elicited erythema in abraded skin and the last two were not irritant

(Campbell et al., 1975). However, $PdCl_2$ - when tested according to the OECD guide-line No.404 - produced primary irritation also on intact skin and was classified (according to the Draize classification scheme) as a moderate irritant (Johnson Matthey, 1994b). No dermal reactions have been found with $[Pd(NH_3)_4](HCO_3)_2$ applied to intact skin of rabbits according to the same protocol (Johnson Matthey, 1995b). Pd-hydrochloride (formula not specified) was found to cause dermatitis in the skin of rabbits (Kolpakov et al., 1980).

Eye irritation

Severe eye irritation was observed with $PdCl_2$ and $[Pd(NH_3)_4](HCO_3)_2$ (but not with PdO), both deposited on the eye surface of rabbits (Hysell et al., 1974; Johnson Matthey, 1995c,). Inhalation exposure of rats to chloropalladosamine ($PdCl_2(NH_3)_2$, > 50 mg/m^3) affected the mucous membranes of the eyes of rats (conjunctivitis or keratoconjunctivitis) (Roshchin et al., 1984).

Sensitization

An important health hazard of Pd is its sensitization potential. Some Pd compounds have been proved to be potent sensitizers of the skin: $PdCl_2$ (Boman & Wahlberg; 1990; Wahlberg & Boman, 1990, 1992), $[Pd(NH_3)_4](HCO_3)_2$ (Johnson Matthey, 1997c), Pd hydrochloride (Kolpakov et al., 1980) and Pd-albumin complexes (Taubler, 1977). $PdCl_2$ was even a stronger sensitizer than the common allergen $NiSO_4$ in the guinea pig maximization test (Wahlberg & Boman, 1990).

Several studies addressed the question of cross-reactivity between Pd and other metals (Wahlberg & Boman, 1992; Liden & Wahlberg, 1994; Wahlberg & Liden, 1999). Guinea pigs induced with $NiSO_4$, chromate or cobalt salts did not react after challenge with $PdCl_2$. However, if induced with $PdCl_2$, they reacted to $NiSO_4$. A possible significant Ni-contamination of the Pd salt has been ruled out by chemical analysis (Wahlberg & Boman, 1992; Liden & Wahlberg, 1994). Further experiments with modified protocols (repeated open applications to the skin of guinea pigs) supported this type of cross-reactivity (Pd → Ni) reported above. Divergently, they found also positive reactions to $PdCl_2$ in animals sensitized with $NiSO_4$. Thereby it remained unclear, if the observed additional reactivity (Ni → Pd) was due to cross-reactivity or to the induction of sensitivity by the repeated treatments (Wahlberg & Liden, 1999).

Indications of cross-reactivity were also seen in *in vitro* studies with metal-specific lymphocytes. Ni-reactive human T-lymphocytes showed cross-reactivities with Pd and Cu salts, but not with other metals more remotely localized in the periodic table of elements (Moulon et al., 1995; Pistoor et al., 1995; Rustemeyer et al., 1999).

Respiratory sensitization (bronchospasms) has been observed in cats after iv administration of several complex Pd salts (0.3-3 mmol/kg body weight). It was accompanied by an increase in serum histamine (Tomilets & Zakharova, 1979).

In general, the animal data are consistent with findings in humans indicating sensitization to Pd, mainly from exposure to Pd-containing dental alloys and jewelry, but also from occupational or unknown exposure (Kielhorn et al., 2002; WHO, 2002; Orion & Wolf, 2005, this book)

Immunotoxicity

Significant immune responses have been obtained with $PdCl_2$ and/or chloropalladates using the popliteal and auricular lymph node assay in BALB/c mice (Kulig et al., 1995; Schuppe et al., 1998)). Preliminary data in an *in vitro* model suggest that Pd(II) and Pd(IV) compounds may be involved in induction of an autoimmune disease (Griem & Gleichmann, 1995). Further special animal studies are lacking, but an epidemiological study reported a possible association between Pd and diseases of the thyroid and the immune system in humans (Helm, 2002).

Carcinogenicity

Despite the increasing Pd exposure of humans from different scenarios, there is a lack of adequate experimental data on possible long-term health effects. However, there are some efforts to discuss the potential for combined evaluation of some metals including Pd, in the absence of metal-specific data on carcinogenicity (IARC, 2003).

Elemental palladium

Up to date, no carcinogenicity studies after inhalation exposure to Pd particles are available.

Subcutaneous implantation of an Ag-Pd-Au alloy led to formation of tumours (fibrosarcoma, myosarcoma, fibroma, and fibroadenoma) at the implantation site in 7 of 14 rats after 504 days. However, it was not clear, if the observed carcinogenicity was due to the chemical components or due to the chronic physical stimulus of the alloy imbedded (Fujita, 1971).

Pd compounds

For Pd compounds only one animal experiment, with some limitations, has been performed. White Swiss Charles River CD mice were exposed for a lifetime via drinking water (from weaning to natural death) to $PdCl_2$ at 5 mg Pd^{++}/litre (corresponding to about 1.2 mg Pd^{++}/kg body weight/day by assuming a body weight of 0.03 kg and a daily water uptake of 7 ml). They developed tumours in both sexes (19/65 versus 13/80 in control; sex-related distribution not specified). Only one tumour found in the exposed group was not malignant. Most of the malignant tumours were either lymphoma-leukemia types (10 versus 2 in controls) or adenocarcinoma of the lung (6 versus 1 in control). The increase in malignant tumours (18/65 versus 11/80 = 27.7% versus 13.8%) was statistically significant ($p < 0.05$) as compared to the parallel (in time) control group (A). This was not the case in comparison to another smaller (non parallel) control group (B), having differing rates of malignant (6/41 = 14.6%) and total (11/41 = 26.8%) tumours (Schroeder & Mitchener, 1971). Interestingly, there was also a significantly enhanced longevity (mean age of the last 10% of survivors: 815 ± 27.1, versus 696 ± 19.2 days in controls) of the male mice, which in turn may have influenced the tumour rate. Other limitations of this study refer to dosage regimen (only one dose was tested) and protocol (tumour rates are pooled for males and females) (WHO, 2002). Other adverse effects observed in this long-term study included suppression of body weight gain and a significantly higher incidence of amyloidosis in several inner organs of males and females (Schroeder & Mitchener, 1971).

DNA interactions and mutagenicity

DNA interactions

Pd compounds have a high affinity for nucleic acids, as confirmed in many *in vitro* studies.

Experiments with $PdCl_2$ and calf thymus DNA indicated that Pd(II) interacts with both the phosphate groups and bases of DNA (Pillai & Nandi, 1977). Several Pd-organic complexes were observed to form bonds with calf thymus DNA (e.g. Jain et al., 1994) or *Escherichia coli* plasmid DNA (e.g. Matilla et al., 1994). Most of the complexes appear to interact via non-covalent binding, mainly via hydrogen bonding, (Mital et al., 1991; Mansuri-Torshizi et al., 1992a,b; Paul et al., 1993; Jain et al., 1994), but in a few cases indications for covalent binding were seen (Mansuri-Torshizi et al., 1991). These interactions can induce conformational changes in DNA structure (Shishniashvili et al., 1971; Pillai & Nandi, 1977; Navarro-Ranninger et al., 1992, 1993; Matilla et al., 1994; Akdi et al., 2002; Perez-Cabre et al., 2004), DNA cleavage (Suggs et al., 1989) or strand breakage (Liu et al., 1997).

For a long time it was not clear whether the *in vitro* reactions with isolated DNA also apply to cellular systems (WHO, 2002). Recently, preliminary experiments with mammalian cells in culture demonstrated the presence of Pd-induced DNA adducts. The adduct formation was observed after a 24-h incubation of A549 human lung cells towards Pd-particles (particle size: 0.25-0.5 µm) - and was found to be dose- and time-dependent (Hartwig et al., 2002).

Mutagenicity

Almost all mutagenicity tests of several Pd compounds with bacterial or mammalian cells *in vitro* (Ames test: *Salmonella typhimurium*; SOS chromotest: *Escherichia coli*; micronucleus test: human lymphocytes) gave negative results (Suraikina et al., 1979; Uno & Morita, 1993; Johnson Matthey, 1995d; Bünger et al., 1996; Bünger, 1997; Gebel et al., 1997; Lantzsch & Gebel, 1997) or quite weak effects (Migliore et al., 2002). As an exception, $[Pd(NH_3)_4](HCO_3)_2$ induced a clastogenic response to human lymphocytes *in vitro*; the increases in the frequency of cells with chromosomal aberrations were statistically significant, but non-dose-related (Johnson Matthey, 1997d). The same compound did not produce positive results in an *in vivo* genotoxicity test (micronucleus test in the mouse, given single oral doses of 125 to 500 mg/kg body weight) (Johnson Matthey, 1998).

There are no studies available focusing on DNA damage or mutagenicity of Pd particles.

Antineoplastic potential

Certain Pd-organic complexes have an antineoplastic potential. A series of different Pd complexes has been designed (mainly since 1986) and screened for cytostatic activity in order to obtain new anticancer drugs having similar activity as *cis*-platinum (a popular agent for the therapy of various human tumours, especially ovarian, testicular or bladder cancers)- *cis*-dichloro-2,6-diaminopyridine-platinum(II) – but less adverse side-effects (WHO, 2002; Kruszewski et al., 2003).To date, only few complexes have been tested *in vivo* in animals (Castan et al., 1990; Trevisan et al., 2002), and none has yet proven sufficiently suitable to warrant clinical trials in humans (Trevisan et al., 2002).

Miscellaneous adverse effects at the (sub-)cellular level

Pd and its compounds have been investigated in numerous *in vitro* studies, which are summarized below. They demonstrate the potential reactivity of Pd species.

Enzyme inhibition

Possibly, some clinical effects of Pd compounds are mediated by enzyme inhibition. A series of isolated enzymes from different living systems (mammals, birds, fish, fungi) and with key metabolic functions have been found to be inhibited by single and complex Pd salts (Spikes & Hodgson, 1969; Christensen, 1971/72; Holbrook et al., 1976; Rapaka et al;. 1976; Liu et al., 1979a,b,c; Christensen & Olson, 1981; Lassig et al., 1995). The strongest inhibition (K_i value for $PdCl_2$ = 0.16 µmol/litre) was found for creatine kinase, an important enzyme of energy metabolism (Liu et al., 1979b). Experiments with elemental Pd have not been located.

Effects on other cellular functions

Pd compounds

There are numerous *in vitro* studies on the cytotoxic effects of $PdCl_2$ (Hussain et al., 1977; Nordlind, 1986; Clothier et al., 1988; Wataha et al., 1991; Nordlind & Liden, 1993; Schedle et al., 1995; Wataha et al., 1995; Schmalz et al., 1997a), $PdSO_4$ (Rapaka et al., 1976), several inorganic/organic Pd-complexes (Kolesova et al., 1979; Aresta et al., 1982; Mital et al., 1992; Bünger et al., 1996; Bünger, 1997) and an undefined Pd^{++} compound (Eimerl & Schramm, 1993; Chiu & Liu, 1997). These studies indicate that Pd ions are capable of inhibiting most major cellular functions. Cytopathogenic effects observed included inhibition of DNA synthesis (Nordlind, 1986; Wataha et al., 1991; Nordlind & Liden, 1993; Schedle et al., 1995) or RNA synthesis (Mital et al., 1992), inhibition of protein synthesis or decrease in total protein content or mitochondrial activity (Clothier et al., 1988; Wataha et al., 1991 and 1995; Schmalz et al., 1997a), necrosis (Schedle et al., 1995), reduction of cell viability (Bünger et al., 1996; Bünger, 1997), loss of membrane integrity (Wataha et al., 1995), inhibition of macrophages chemotaxis (Aresta et al., 1982), potentiation or inhibition (depending on concentration) of glutamate toxicity (Eimerl & Schramm, 1993), inhibition of respiration and ATPase activity (Kolesova et al., 1979) or changes in collagen synthesis processes (Rapaka et al., 1976; Hussain et al., 1977). DNA/RNA biosynthesis seems to be a very sensitive target. An EC_{50} value of $PdCl_2$ for inhibition of DNA synthesis *in vitro* with mouse fibroblasts was 300 µmol/litre (32 mg Pd^{++}/litre) (Wataha et al., 1991). An inhibition of DNA synthesis was also observed *in vivo*, e.g. in spleen, liver, kidney and testes of rats given single intraperitoneal doses of 14 - 56 µmol/kg body weight (1.5 - 6 mg Pd^{++}/ kg body weight) of $Pd(NO_3)_2$ (Fisher et al., 1975).

Mediators of inflammation like prostaglandins and interleukins have been found to be released in response to $PdCl_2$ even under nontoxic experimental conditions *in vitro* (Schmalz et al., 2000). Some Pd salts ($PdCl_2$, $(NH_4)_2[PdCl_6]$, $(NH_4)_2[PdCl_4]$) are capable of influencing lymphocyte proliferation and cytokine release *in vitro* (Boscolo et al., 2004). $PdCl_2$ was involved in the production of ROS (reactive oxygen species) by human neutrophils *in vitro* (Theron et al., 2004). If operative *in vivo*, such interactions may play a role in pathogenesis.

Elemental palladium

Pd applied in its metallic form (incubation of small test pieces) showed no (Kawahara et al., 1968); Schmalz et al., 1997b, 1998) or little (Kawata et al., 1981; Niemi & Hensten-Petersen, 1985) cytotoxicity, but induced an 4-fold increase in interleukin-6 levels compared with untreated controls (Schmalz et al., 1997b, 1998).

Pd-containing alloys tested varied in their *in vitro* cytotoxicity, depending mainly on microstructure and composition of the samples (Kawahara et al., 1968; Kawata et al., 1981; Niemi & Hensten-Pettersen, 1985; Ito et al., 1995; Warocquier-Clerout et al., 1995). Severe effects seem to be triggered by other components (e.g. Cu).

Mode of action

It is assumed that at least for processes in the oral cavity, ions can be formed from metallic Pd in dental restorations, leading to solution in the saliva and finally to distribution in the body. Fine particles of Pd may also be taken up by epithelial cells or lymphocytes and macrophages, etc. and be transported within the lymphatic system. Pd ions can interact with a multitude of cellular processes and thus disturb them. Complex formation of Pd ions with cellular components probably plays a basic role initially. Oxidation processes may also be involved - due to the different oxidation states of Pd (WHO, 2002).

5.4.3 Summary and conclusions

Under certain conditions, release of Pd ions (and possibly microparticles) from metallic Pd appears to be possible, but quantitative data are missing. There are also indications that very finely dispersed elemental Pd particles become bioavailable, when in contact with biological media. Pd ions can be taken up by the skin or by oral and inhalative routes. Although absorption and retention are poor, there may be a risk for sensitized or sensitive individuals. Principally, absorbed Pd can be found in almost all organs, tissues or body fluids of experimental animals.

Pd and its compounds are of very low to moderate acute toxicity if ingested (depending mainly on their solubility). The inner organ most consistently affected after single and repeated exposures seems to be the kidney. An increase in amyloidosis of several inner organs has been found in the only available life-time study (with mice given $PdCl_2$ in drinking water). Some general toxic effects, e.g. delayed body weight gain, changes in clinical parameters or pathological changes in inner organs, have been recorded not only following oral doses of Pd salts, but also after oral treatment with elemental Pd.

A 28-day guideline study reported a NOAEL of 1.5 mg tetraammine palladium hydrogen carbonate/kg body weight per day (corresponding to 0.54 mg Pd/kg body weight per day) in rats after oral dosing. This value referred to histopathological end-points in inner organs. However, absolute organ weight changes yet occurred at this dose level.

Several Pd salts cause severe primary skin and eye irritation. The most important target was the immune system, as demonstrated by *in vitro* and animal tests. Pd ions have been shown to be potent skin sensitizers, with cross-reactivity to Ni possible. There have been also some indications of a potential for respiratory sensitization (bronchospasms in cats). The sensitization risk is of serious health concern, especially because very low doses are sufficient to cause allergic reactions in susceptible individuals. For this reason, the WHO has recommended to be restrictive in using Pd in dental alloys.

The carcinogenic risk from oral exposure to Pd salts or through Pd-containing metallic implants remains unclear. The two studies available reported an increased incidence of tumours, but both had considerable limitations. Carcinogenicity studies after inhalation exposure have not been performed, although Pd-containing particles are generated in workplaces or in the ambient air from automobile catalysts.

Pd salts did not show mutagenicity in bacterial test systems. However exceptionally, weak effects were seen *in vitro* with mammalian cells. Interaction with DNA occurred *in vitro*. DNA synthesis was found to be inhibited *in vitro* and *in vivo*. A series of further cytotoxic effects has been documented for Pd salts *in vitro*, with enzyme inhibition being prevalent. Some Pd complexes had also an antineoplastic potential. Little *in vitro* cytotoxicity has been elicited by metallic Pd. Suitable data on reproductive and developmental toxicity are missing.

In summary, some features of Pd toxicity are apparent, but further data are necessary to complete the toxicological profile of Pd qualitatively and quantitatively. Actually, health hazards from inhalation of Pd dust cannot be evaluated due to lack of toxicological data. However, the use of Pd in dental alloys and jewelry may pose a health risk for the general population.

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Author Index

Subject Index