THE ENVIRONMENTAL RELEVANCE OF THE PLATINUM GROUP ELEMENTS

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Platinum group elements (PGE) are used in an increasing number of applications and emissions are causing an increase in the environmental concentrations of these normally rare metals. Automobile exhaust catalysts, which use Pd, Pt and Rh as active components, are the main source of PGE into urban and roadside environments, and contribute to a global increase in PGE concentrations. Emitted PGE are found in urban air and accumulate on the road surface and in roadside soil. Transport of PGE through stormwater is providing an increasing contamination of aquatic environments. There is now increasing evidence that a fraction of PGE in the environment is bioavailable and potential uptake into the biosphere is raising concern over potential risks for man and the environment.

This review describes the emissions, distribution, physico-chemical forms, bioavailability and toxic effects of PGE emitted by automobile catalysts and other sources. Important features and future trends are discussed.

INTRODUCTION

Platinum group elements (PGE; i.e. Ir, Os, Pd, Pt, Rh, Ru) are concentrated in the Earth's core and mantle with low natural abundances in the continental crust. Average upper continental crust concentrations range from 0.02 ng g^{-1} for Ir to 0.5 ng g^{-1} for Pt and Pd and represent <0.01% of the Earth's PGE budget. As a result, the cycling of PGE in surface environments is limited in importance and associated risks for man and the environment are generally considered to be inconsequential. However, reports of increasing PGE concentrations in the environment are raising concern that this situation is changing.

Worldwide PGE production has steadily increased since the 1970s to supply their increasing use in applications including automobile exhaust catalysts, industrial process catalysts, jewelry, dental implants and electronics (Figure 1). The subsequent release of PGE into the

environment is causing a redistribution of PGE and increasing concentrations of these elements have been reported in surface environments. It is now important to assess the potential impacts of this new contamination on man and the environment. This review presents the current knowledge on PGE emissions, accumulation, dispersion and impacts.
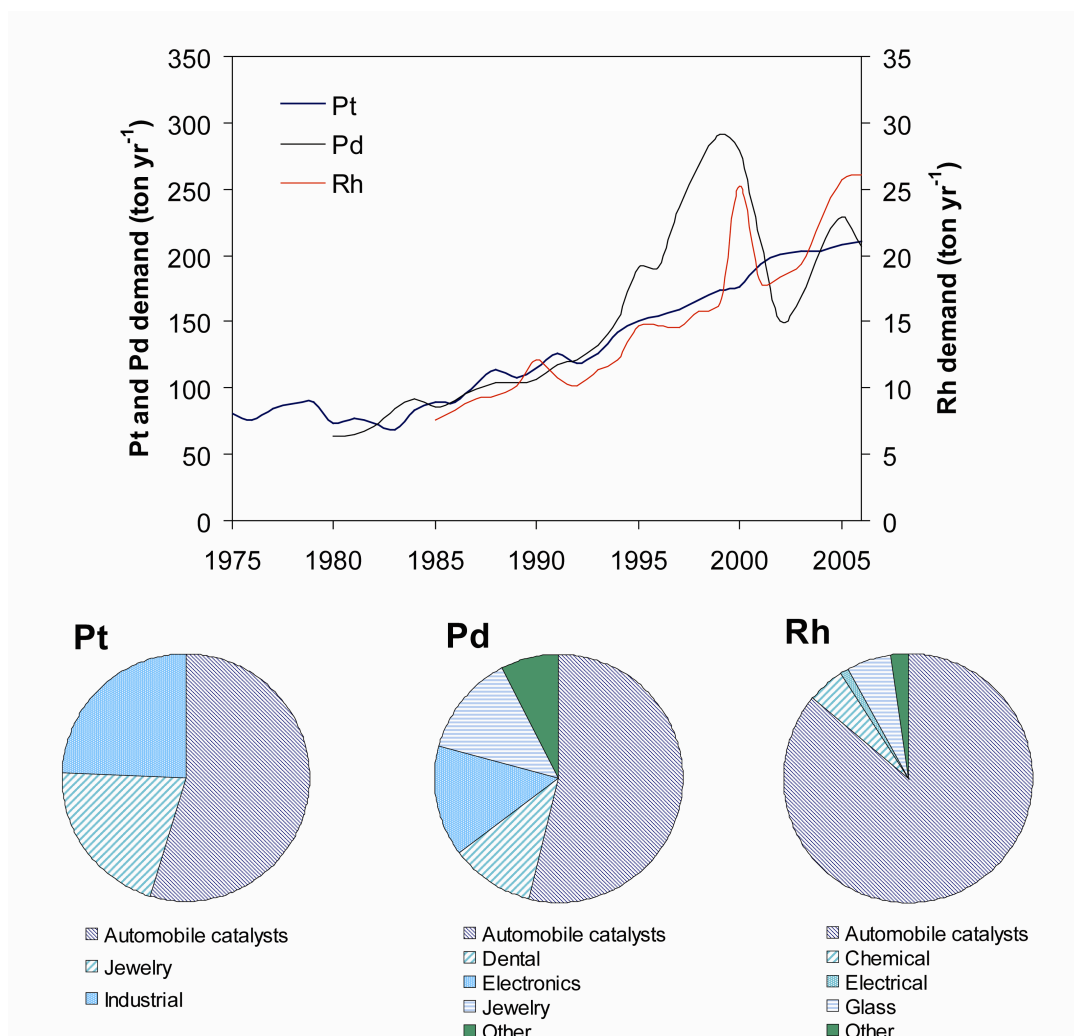

Figure 1. Changes in total Pt, Pd and Rh demand for 1975-2006 and distribution by sectors for 2006 (source Jonhson Matthey, 2007).

ANTHROPOGENIC PGE EMISSIONS

PGE emissions might occur during PGE production, manufacture of PGE-containing products and use and disposal of these products. At present, the only documented anthropogenic PGE sources are metal production (Niskavaara et al., 2004; Rodushkin et al., 2007), automobile exhaust catalysts (Artelt et al., 1999a; Moldovan et al., 2002) and medical applications (Esser and Turekian, 1993; Kummerer et al., 1999). Although additional sources of PGE to the environment may exist, they have not been characterized or reported to date.

PGE emissions from automobile catalysts

Automobile catalysts are generally believed to be the main source of PGE into the environment. These catalysts use Pd, Pt and Rh to promote the removal of gaseous pollutants in vehicle exhausts and a fraction of the PGE in catalysts is emitted into the environment during vehicle operation (Moldovan et al., 2002). In addition, catalysts contain Os, Ir and Ru impurities and these metals are released into the environment alongside Pd, Pt and Rh (Fritsche and Meisel, 2004; Poirier and Gariepy, 2005; Rauch et al., 2004a). Direct measurements of PGE emissions from automobile catalysts provide emission estimates in the ng km^{-1} range. Emissions from gasoline catalysts are expected to be in the low ng km^{-1} range, whereas a 10-100 fold higher Pt emissions have been measured for diesel catalysts (Moldovan et al., 2002). In contrast, an emission rate of 0.8 µg km^{-1} has been inferred from indirect measurements based on the analysis of environmental samples and traffic information (Helmers, 1997). This higher emission estimate has been attributed to conditions encountered in real life, e.g. engine ignition problems, that are not taken into consideration in bench tests used for direct measurements. Emission rates depend on factors including engine and catalyst types, PGE content in the catalyst, mileage of the catalyst, engine condition, vehicle speed and driving conditions (Ravindra et al., 2004). A global catalyst emission of 0.8-6.0 metric tons of Pt year^{-1} can be inferred assuming that 500 million vehicles are equipped with catalysts with an average yearly mileage of 15 000 km vehicle^{-1} and an average emission rate of 0.1-0.8 µg km^{-1} (Rauch et al., 2005).

The emission mechanism and the form of PGE in automobile exhaust are still unclear. It is generally believed that mechanical erosion of the catalysts surface is the major cause for PGE emissions, although thermal and chemical processes may also contribute to PGE emissions. Pd, Pt and Rh occur in particles sizes ranging from sub-micron to >63 µm in automobile exhaust and in the urban environment, supporting that emission is a combination of processes including chemical and thermal ageing. In addition, chemical transformation is supported by the occurrence of soluble PGE in automobile exhaust. Whereas soluble Pt represents less than 10% of total Pt emissions, soluble Pd and Rh fractions might be larger than 50% of total emissions. The occurrence of fine PGE-containing particles and soluble PGE species in the environment raises concern over potential environmental and health risks.

PGE emissions from mining and metal production

Metal production in Northern Europe has also been reported to result in PGE emissions. Nickel smelters in the Kola Peninsula in NW Russia have been identified as an important regional source of Pt and Pd based on the spatial distribution of these metals in environmental samples (Niskavaara et al., 2004). Chromium smelters in the Kemi district in Finland have been identified as a source of Os (Rodushkin et al., 2007). However, emission rates have not been determined and data for other metal production sites are needed to assess the extent of PGE emissions by metal production activities. Further, emissions from PGE production activities in South African, the leading PGE producer, need to be determined.

PGE emissions from medical facilities

Platinum-containing drugs, including cisplatin (cis-diammine-dichloroplatinum(II)) and carboplatin (diamine(1,1-cyclobutanedicarboxylato)platinum(II)), are used in the treatment of several forms of cancer. Platinum is excreted by the patients after administration of Pt-based drugs and is found in hospital effluents at concentrations ranging from <10 ng l^{-1} to 3.5 μg l^{-1}, but Pt is diluted in the municipal wastewater system and concentrations are <10 ng l^{-1} in sewage effluents (Kummerer et al., 1999). Emission is expected to be in form of soluble compounds including administered drugs and their derivatives. Osmium is also believed to be emitted from medical facilities where it is used as a stain fixative in electron microscopy applications (Esser and Turekian, 1993).

Other potential anthropogenic sources

Today PGE are used in a wide range of applications and emissions might occur during PGE production, manufacture of PGE-containing products and use and disposal of these products. Although emissions from PGE production and manufacture are expected to be limited or relevant to specific sites, the use and disposal of PGE-containing items are of concern because of the potential leaching of PGE. Emissions from these sources have however not been determined.

The contribution of natural sources, including erosion and volcanic emissions, and the potential impact of human activities on some natural sources also need to be investigated. Increased erosion resulting from agriculture or deforestation may for instance contribute to elevated concentrations at remote sites where no direct anthropogenic sources are present.

PGE ACCUMULATION AND DISPERSION

PGE emissions into the environment are causing an increase in the concentrations of these normally rare metals. Most studies to date have focused on roadside and urban sites, where elevated Pd, Pt and Rh concentrations have been attributed to automobile catalyst emissions. Typical concentration ranges are presented in Figure 2. Automobile catalysts emissions are also believed to be responsible for elevated Ir, Os and Ru owing to the occurrence of these elements as impurity in catalysts (Fritsche and Meisel, 2004; Rauch et al., 2004a).

Regional and long-range transport - accumulation in remote environments

Air particles
Pt: 4-20 pg m^{-3}
Pd: 2-20 pg m^{-3}
Rh: 0.3-5 pg m^{-3}

Possible biological uptake

Road dust
Pt: 50-300 ng g^{-1}
Pd: 10-300 ng g^{-1}
Rh: 10-60 ng g^{-1}

Roadside soil
Pt: 25-250 ng g^{-1}
Pd: 1-12 ng g^{-1}
Rh: 4-40 ng g^{-1}

Urban water
Pt: 1-10 ng l^{-1}
Pd: 10-50 ng l^{-1}
Rh: - ng l^{-1}

Stormwater

Coastal environment

Sediments
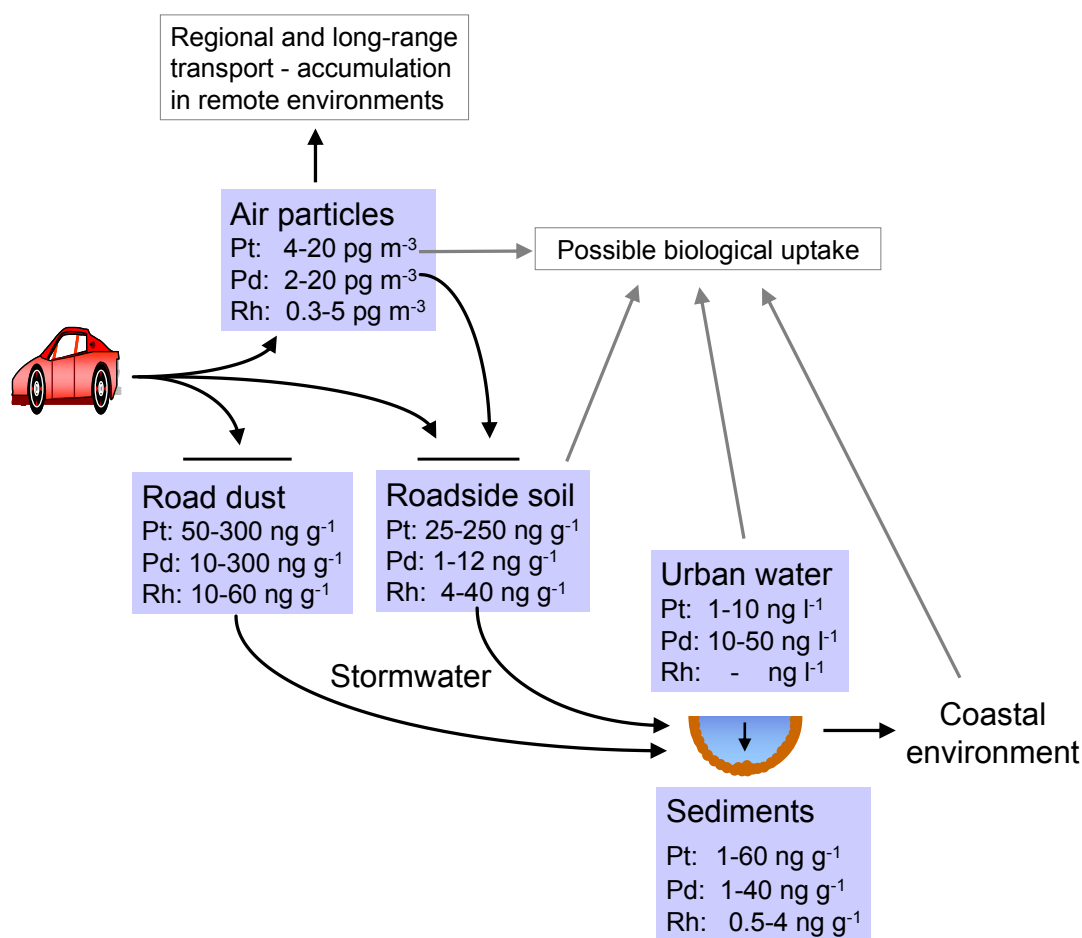Pt: 1-60 ng g^{-1}
Pd: 1-40 ng g^{-1}
Rh: 0.5-4 ng g^{-1}

Figure 2. The fate of PGE from automobile catalysts in the urban environment. Concentration range typically found for selected compartments (compiled from general literature data) are provided.

Emitted PGE are found in airborne particles where they occur at the pg m^{-3} level (Ravindra et al., 2004). The concentrations of Pt and Rh in airborne particles increased 46 and 27 fold over a 10-year period (1988-1998) near a heavy traffic road in Germany (Zereini et al., 2001). Particles deposit on the road surface or roadside soil with decreasing concentration at increasing distance from the road. During rain events the accumulated PGE can be transported to rivers or water bodies where they accumulate in sediments, while concentrations in water remain low. An increase in Pd, Pt and Rh deposition was found in lake sediments in the USA, where deposition increased 15, 8 and 6 fold, respectively, following the introduction of automobile catalysts (Rauch et al., 2004a). Further transport of sedimented PGE through resuspension might also result in the contamination of coastal environments. Input from medical facilities due to combine sewer overflow might be an additional source of PGE in the aquatic environment, but it is expected to be of limited importance relative to the automobile catalyst input.

While the highest occurrence remains in the urban and roadside environment, a significant fraction of PGE emitted by automobile catalysts is dispersed at regional and global scales owing to their occurrence in fine particles (Rauch et al., 2005). PGE are found in particles with diameters ranging from < 1 μm to over > 63 μm (Gomez et al., 2002); whereas relatively large particles are expected to deposit close to their source, a significant fraction of PGE containing particles in automobile emissions has a sufficiently long atmospheric residence time to be transported over long distances (Rauch et al., 2005). Elevated PGE concentrations at remote sites support a widespread atmospheric dispersion of emitted PGE (Barbante et al., 2004; Barbante et al., 2001; Rauch et al., 2004b). Increasing PGE concentrations have been reported as far from automobile traffic as Central Greenland (Barbante et al., 2001). Although recent results raise concern over the validity of reported Greenland concentrations (De Boni, 2007), the widespread dispersion of PGE is also supported by increasing accumulation in Alpine glaciers (Barbante et al., 2004) and a remote peat bog located approximately 300 m from automobile traffic (Rauch et al., 2004b). In the latter study, Pd, Pt and Rh deposition was determined to be of almost exclusively anthropogenic origin using Os isotopic composition as a proxy for the estimation of natural input.

PHYSICO-CHEMICAL FORMS AND TRANSFORMATION

The chemical form of PGE in the environment depends on the form in which PGE are emitted and subsequent transformations. In the environment, PGE are generally associated with the particle phase as a result of their emission as particles or their interaction with environmental components.

PGE are present as finely dispersed PGE nanoparticles in catalysts and are likely to be emitted in the form of PGE nanoparticles or as washcoat particles (γ-Al$_2$O$_3$) onto which PGE are attached. Sintering may also result in the emission of PGE particles in the μm range. Subsequently different types of PGE-containing particles are expected to be found in the environment, resulting in differences in their environmental reactivity (Figure 3). In addition, soluble PGE species have been found in automobile exhaust. There is however no clear agreement on the amount of soluble PGE in automobile exhaust emissions. Moldovan et al. (2002) reported that the soluble fraction represents approximately 10% of total Pt emissions, while as much as 40% of Pd and Rh may be soluble in a weak acid solution. The remaining fraction is expected to be in a metallic form. Because soluble is defined as <0.45 μm, the
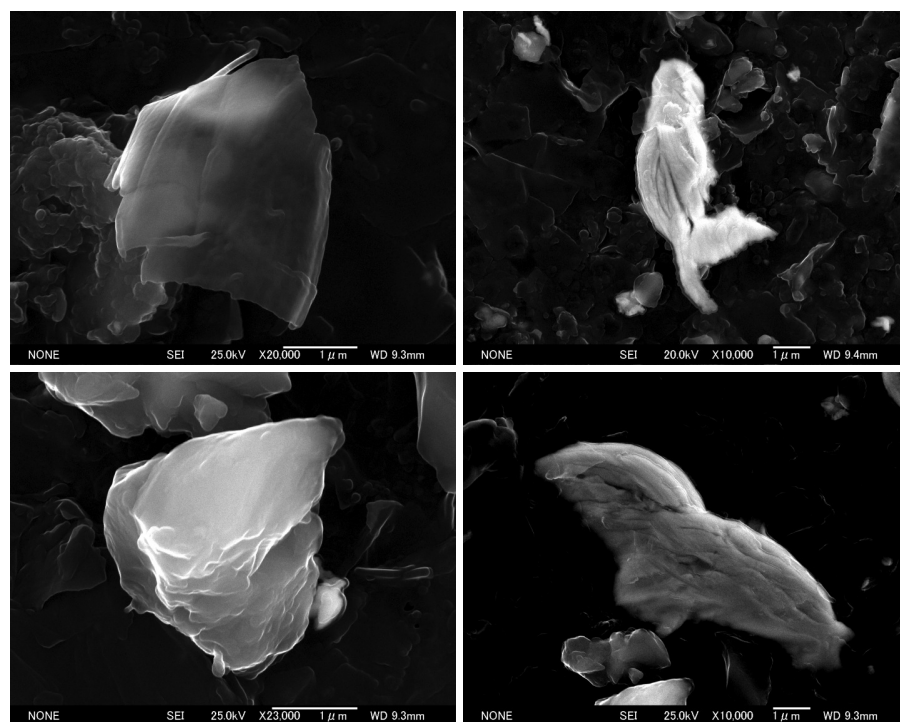

Figure 3. Field emission scanning electron microsopy images of PGE containing particles in urban air in Göteborg, Sweden. (Photos 1, 3 and 4 reproduced with permission from *Environ. Sci. Technol.* 2005, *39*, 8156. Copyright 1998 American Chemical Society; Photos courtesy of M. Owari, University of Tokyo, Japan)

soluble fraction may also include PGE nanoparticles. Hospital emissions are an additional source of soluble Pt into the aquatic environment, with the emission of platinum-based drugs and their derivatives resulting from patient excretion.

Particle size and especially the occurrence of PGE as nanoparticles may also play a major role in the presence and formation of soluble PGE species. As mentioned earlier, soluble PGE may include nanoparticles if the soluble fraction is estimated by filtration at <0.45 μm. In addition, fine particles have relatively large surface areas and offer more possibility for reactions with environmental substances. Larger particles are likely to be composed of catalyst washcoat and PGE nanoparticles may be released under conditions which promote the dissolution of γ-Al_2O_3.

PGE in automobile emissions are predominantly in a metallic form. Metallic PGE are usually considered to be inert and environmentally unreactive and it may be reasoned that they cannot be oxidized. Oxides and hydroxide forms also have a limited solubility. Studies on the solubility of PGE provide an uncertain picture of the amount of soluble PGE compounds in the environment. Differences are likely due to the form of PGE in different environmental compartments, as well as the presence of reaction promoters and the readsorbtion of soluble PGE onto solid surfaces. It is however clear that Pd has a higher solubility than Pt and Rh (Jarvis et al., 2001; Moldovan et al., 2001). Naturally occurring complexing agents may play an important role in the solubilization of PGE and their fate in the environment. Such complexones are widely found in many soils and freshwater systems. The presence of humic acids, as well as triphosphate, pyrophosphate and L-methionine, increases the solubility of platinum (Lustig et al., 1998). Siderophores (organic ligands secreted by microbes and plants to extract metal nutrients from soil) also have the potential to solubilize PGE metals and oxides, thereby increasing their environmental mobility and enabling their uptake by plants (Normand and Wood, 2005; Dahlheimer et al., 2007). The extraction of PGE is in the order Pd>Pt>Rh (Dahlheimer et al., 2007). Experiments on the interactions of PGE with humic soils indicate that Pt is subject to complex transformations in soil. Pt is oxidized and released from the particle surface by a complexing agent, leaving the surface free for further oxidation (Lustig et al., 1996). However, the formation of organic complexes may also explain the relatively low mobility of PGE in soils (Lustig et al., 1996).

Emitted PGE particles may reach aquatic environments, where they are expected to remain largely insoluble. The soluble fraction may react with particles or form complexes with inorganic or organic ligands. The input of particulate or particulate reactive PGE to aquatic

systems has been demonstrated using sediment cores (Rauch et al., 2004a). A study on the behavior of soluble PGE in river water showed that a significant fraction of PGE binds to particulate matter (>45 μm). The speciation of Pt, Pd and Rh is controlled by different mechanisms. Palladium is complexed by small hydrophobic organic ligands (<0.1 μm); Rh is complexed to these organic ligands, but also forms hydroxychlorides; Pt forms inorganic aqueous species and the particle-water reactivity of Pt is controlled by electrostatic interactions (Cobelo-Garcia et al., 2008). The bahavior of PGE in natural waters results in increasing solubility in estuarine mixing (Cobelo-Garcia et al., 2008).

BIOAVAILABIlITY AND TOXIC EFFECTS

The emission of PGE and increasing environmental concentrations raises concern over the potential risks of this contamination for man and the environment. Risk depends on exposure, bioavailability and toxicity.

Uptake by flora and fauna

Transformation of PGE and the occurrence of soluble species in the environment indicate that a fraction of PGE is a bioavailable form. It follows that exposure to PGE may result in uptake and eventually toxic effects.

Roadside vegetation is exposed to relatively high PGE concentrations owing to proximity to automobile traffic. Elevated PGE concentrations have been found in roadside grass (Zimmermann and Sures, 2004). However, elevated concentrations are largely due to PGE deposition on the plant surface and actual uptake from soil is relatively limited, possibly due to exposure routes with atmospheric deposition being the largest source of PGE to the grass. Accumulation of PGE on the plant surface is likely the result of particle adsorption. PGE uptake from soil has also been demonstrated in laboratory experiments and may contribute to internal PGE accumulation (Zimmermann and Sures, 2004). The uptake mechanism is believed to be linked to complexones (siderophores) used by plants for the extraction of metallic nutrients from soil. Highest concentrations are generally found in the roots, followed by the shoots and the leaves, indicating uptake but limited transport in the plants (Zimmermann and Sures, 2004).

Aquatic organisms have been reported to take up and accumulate PGE under environmental conditions. Freshwater benthic organisms were found to contain 38.0 ng g^{-1} Pt, 155 ng g^{-1} Pd and 17.9 ng g^{-1} Rh. These organisms feed on sediments and the uptake route is believed to be dietary intake and dissolution of PGE in the digestive system (Moldovan et al., 2001).

Laboratory exposure supports that PGE are present in a bioavailable form in the aquatic environment and can be taken up by aquatic fauna, including invertebrate and fish species (Zimmermann and Sures, 2004).

Studies on higher organisms are scarce. Exposure of rats to model Pt containing particles resembling automobile emissions support that Pt can be taken up through inhalation or intratracheal intake (Artelt et al., 1999b). A substantial fraction of Pt was found to be bioavailable as a result of *in vivo* solubility. Increased concentrations were found in the blood, urine and feces, as well as tissues including the liver, spleen, kidneys, stomach, adrenal and femur. Over 90% of the bioavailable Pt is bound to proteins and the remaining fraction possibly corresponds to low molecular weight ionic complexes (Artelt et al., 1999b).

In general, Pd is found to be more bioavailable than Pt and Rh. Experimental studies also reveal that uptake and accumulation depend on the chemical speciation of PGE in the environment (Zimmermann and Sures, 2004); at present, knowledge on the chemical form of PGE in the environment is very limited. Binding to proteins is believed to play a major role in PGE accumulation in organisms (Zimmermann and Sures, 2004). Further characterization of PGE in the environment and in the biosphere is needed to understand uptake and accumulation mechanisms.

Human exposure and health effects

Human exposure to PGE is expected to be through inhalation of fine PGE-containing particles, skin contact and dietary intake. Human exposure and uptake have been investigated in studies comparing populations with different exposure to automobile traffic. Adults from a large city with dense traffic have larger urinary Pt and Rh concentrations than adults from a smaller town with relatively low traffic, but no clear trend was found for Pd (Bocca et al., 2004). In contrast a significant correlation between urinary concentrations and traffic density was found in children for Pd and Rh, but no correlation could be found for Pt (Caroli et al., 2001). Despite some inconsistencies, these studies clearly show that human exposure, possibly through inhalation, results in the uptake of PGE although PGE may not be transferred to organs.

Reported toxic effects observed at high concentrations in medical and occupational studies include sensitization (Pt and Pd salts), mutagenic effects in bacterial and mammalian cells (soluble Pt compounds), and increased tumor incidence ($PdCl_2$ and $RhCl_3$). Effects of PGE have been observed for high exposure in medical or occupational settings. However, effects have not been determined under environmental conditions as concentrations are generally

considered to low for any effect to occur. While a no-effect limit concentration of 1.5 ng m^{-3} has been set for exposure to Pt salts in a catalyst manufacturing plant (Merget and Rosner, 2001), airborne Pt concentration typically do not exceed 100 pg m^{-3} and only approx. 10% may be in the form of soluble salt. Available data on Pd and Rh are still insufficient to determine the likelihood of potential effects on human health, but effects from PGE exposure in the environment are considered unlikely (Merget and Rosner, 2001). Further characterization of exposure, uptake and effects are needed.

CONCLUSION

Reports of elevated PGE concentrations and uptake by biota are raising concern over the potential risks of PGE emissions by automobile catalysts and other sources. Emissions are expected to increase in the near future owing to increasing PGE loading resulting from increasingly stringent emissions regulations in developed countries and the introduction of catalysts in developing countries. New uses for PGE may also result in additional emissions. Ru demand for consumer electronics (hard drives and plasma screens) has soared in recent years and increased emission of this metal may also occur in the future.

Despite increasing concentrations, current environmental PGE levels remain low and risks for man and the environment are therefore expected to be limited. It is however important to stress that presently available data are not sufficient for an accurate assessment of potential risks. Studies on the effects of PGE are sparse and do not generally provide environmentally relevant information; studies on chronic effects at low exposure concentrations are insufficient at present. The physico-chemical form of PGE, including the occurrence of PGE as nanoparticles, and the higher bioavailability of Pd need to be taken into consideration.

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