

Review:

**Platinum group elements in the environment and
their health risk**

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Abstract

Accumulation of platinum group metals (PGMs) is increasing in the environment over the time. Catalytic converters of modern vehicles are considered to be the main sources of PGM contamination, since the Pt:Rh ratio of around 5 in various environmental compartments reflects the ratio in converter units. The present literature survey shows that the concentrations of these metals have increased significantly in the last decades in diverse environmental matrices; like airborne particulate matter, soil, roadside dust and vegetation, river, coastal and oceanic environment. Generally, PGMs are referred to behave in an inert manner and to be immobile. On the other hand, there is an evidence of spread and bioaccumulation of these species in the environment. Platinum content of road dusts, however, can be soluble, consequently, it enters to the waters, sediments, soil, and finally, the food chain. The effect of chronic occupational exposure to Pt compounds is well-documented, and certain Pt species are known to exhibit allergenic potential, but the toxicity of bioavailable anthropogenic Pt is not clear. Hence there is a need to study the effect on human health of long-term chronic exposure to low levels of Pt compounds.

KeyWords: *Platinum Group Elements, Environmental Matrices, Health risk, Sensitizer*

Introduction

The increasing use of platinum group metals (PGMs) in vehicle catalytic converters, in addition to some other application (e.g. industrial, jewelry, anticancer drugs, etc.), leads to the emission of PGMs into the environment. These metals are naturally found at very low concentration in the earth crust, but the anthropogenically increasing concentration poses a risk to living organisms and human beings. Barbante et al. (2001) have roughly estimated that the annual Pt emission only from catalytic converters may be 0.5-1.4 ton yr⁻¹. These calculations are based on an emission factor of 65-180 ng km⁻¹ from automobile sources and considering that there are about 500 millions cars worldwide equipped with catalytic converter and that the averaged mileage is about 15000 km per year. The recycling of catalytic converters will also increase the emission. Each year approximately 10 million automobiles are scrapped only in the United States and based on the equivalent number of converters, it is also estimated that 155 ton of platinum and 62 ton of palladium, and 16 ton of rhodium will be wasted annually (Gaita and Al-Bazi, 1995).

PGM contamination initially occurs in airborne particle, roadside dust, soil, sludge, and water, etc.; finally it results in bioaccumulation from these sources through diverse pathways. There are several studies on the increasing PGM concentration in human body fluids and tissues exposed to the occupational environment (e.g. precious metal refinery workers). The metallic form of these elements is considered to be inert for biological reactions, but in contrast some platinum salts like hexachloro platinate and tetrachloro platinite are among the most potent allergens and sensitizers. PGMs have also been found to be related to asthma, nausea, increased hair loss, increased spontaneous abortion, dermatitis, and other serious health problems in humans.

Various reviews of this particular topic appeared in the literature; i.e. on: the occurrence and use of PGMs (Rao and Reddi, 2000), the distribution and speciation of PGMs in environmental compartments (Barefoot, 1999), the determination methods of PGMs in environmental samples (Barefoot, 1997; Balcerzak, 1997; Barefoot and Van Loon, 1999; Pyrzyńska, 2000; Rao and Reddi, 2000), and the possible health risk of anthropogenic PGMs (Merget and Rosner, 2001).

Considering all the above points, the present paper comprehensively reviews the literature on the topic related to environmental contamination, transportation, transformation, bioavailability, bioaccumulation, and possible health risk related aspects of the platinum group metals.

Platinum group metals

The platinum group metals, sometimes referred as the platinum group elements (PGEs), comprise the rare metals platinum (Pt), palladium (Pd), rhodium (Rh), ruthenium (Ru), iridium (Ir) and osmium (Os). Average concentration of these metals in lithosphere is estimated to be in the region of 0.001-0.005 mg kg⁻¹ for Pt, 0.015 mg kg⁻¹ for Pd, 0.0001 mg kg⁻¹ for Rh, 0.0001 mg kg⁻¹ for Ru, 0.005 mg kg⁻¹ for Os and 0.001 mg kg⁻¹ for Ir (Greenwood and Earnshaw, 1989; Hartley, 1991). PGMs naturally occur in nickel, copper, and iron sulfide seams (Bradford, 1988). These metals are noble, chemically less reactive materials, and can be found in the nature as native alloys, consisting mainly of platinum.

Sources and applications

PGMs are currently mined in South Africa, Siberia and Sudbury, Ontario. Worldwide production of PGMs, of which 40-50 % is platinum, has been steadily increasing since 1970. This reflects the growing worldwide use of PGMs (WHO, 1991). The total worldwide supply in 1999 and 2000 was 138 and 153 tonnes for Pt, 230 and 224 tonnes for Pd, 14.2 and 20.9 tonnes for Rh, respectively (Johnson Matthey, 2001).

Recently, these metals have gained importance as industrial catalysts including in vehicle exhaust catalysts (VECs), due to their exceptional catalytic properties. Other specific properties are particularly the resistance to chemical corrosion over a wide temperature range, high melting point, high mechanical strength, and good ductility, which relate these metals to various applications. Apart from vehicle exhaust catalysts, additional major uses of PGMs are in the chemical, electrical, electronics, and petroleum industries, the manufacture of jewelry, in medicine as a cancer treatment drug, in dentistry as an alloy, and in the glass industry. Since rhodium has been introduced into catalytic converters, approximately 73 % of the world's rhodium production is consumed by the catalyst manufacturing industry (Manziek,

1990). Demands for 1999 and 2000 for these metal are shown by application in Table 1 (Johnson Matthey, 2001). The trends over time in Pt and Pd uses by application for Europe are listed in Tables 2 and 3 (Johnson Matthey, 2001). The growing demand for Pd in Europe is largely in response to the introduction of Euro Stage III legislation from January 2000; ie. the palladium-rich catalysts can meet stricter emission limits for petrol-fueled vehicles, resulting in a further diverging from platinum technology (Johnson Matthey, 2001).

Catalytic converters

A catalytic converter is a unit that fits into the front part of motor exhaust system of a vehicle, close to the engine, to reduce the emission of gaseous pollutants, such as carbon monoxide (CO), nitrogen oxides (NO_x), and hydrocarbons (HC). It is usually fitted with a heat shield to limit internal temperature drops, ie. heat losses (Figure 1). Removal of the pollutant gases from the exhaust of a properly tuned combustion engine take place by either reduction, or oxidization. Combination of heat with the precious metal catalysts facilitates these heterogeneous reactions in the converter. These catalysts convert over 90 percent of CO, HCs and NO_x into carbon dioxide (CO₂), water and nitrogen. Both NO_x and CO are eliminated together by a redox reaction on a rhodium catalyst. NO_x oxidizes CO to CO₂ and is reduced to harmless nitrogen gas (N₂), whilst CO and HC are oxidized by air on platinum catalyst. For all these reactions to happen, the converter is designed as a ‘three-way converter’, and has an oxygen monitor fitted to the engine. The monitor checks the quantity of oxygen entering into the engine to make sure enough oxygen to carry out oxidation reactions.

There are various designs possible for a converter; however, most of them consist basically of a monolithic honeycomb support made of alumina, or cordierite (a phase of 2MgO.2Al₂O₃.5SiO₂), and are housed in a stainless steel box. Generally, a vehicle exhaust catalyst contains around 1-3 g of PGM, corresponding to approximately 1.8 mg cm⁻³ PGM of the catalyst. The honeycomb, made of cordierite, contains 300-400 square channels per square inch (6.45 cm²), and is coated with an activated, high-surface alumina layer, the so-called “washcoat”. The washcoat consists of about 90 % γ-Al₂O₃ and a mixture of base metal additives, mainly oxides of Ce, Zr, La, Ni, Fe, and some alkaline earth metals that improve the performance of the catalyst by acting mainly as promoters of the desired catalytic

reactions, or stabilizers against deterioration and aging. The noble metals (Pt, Pd, and Rh) are fixed in the washcoat surface usually by impregnation, or coating from a solution of hexachloroplatinic (IV) acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$), palladium chloride (PdCl_2), and rhodium chloride (RhCl_3) salts. After the evaporation of the solvent, a dry layer of the PGM salts is resulted in on the surface of the carrier. The next step is the decomposition of the PGM salts and reduction to obtain the highly dispersed, catalytically “active” metallic forms. Nowadays, there is a wide range of possible combinations and concentrations of the above noble metals with base metals in the catalysts, which can be utilized to achieve the different performance characteristics, required in the various vehicle models. In optional Pt, Pd/Rh, Pt/Rh, Pt/Pd, or Pt/Pd/Rh catalysts, the percentage of PGMs with respect to bulk material is less than 0.1 % (w/w). In European gasoline cars, the usual Pt/Rh, or Pd/Rh ratio is around 5 (Farrauto et al., 1992; Heck and Farrauto, 2001; Moldovan et al., 1999). A conventional three-way catalyst typically contains 0.08 % Pt, 0.04 % Pd, and 0.005-0.007 % Rh (Hoffman, 1989).

Catalytic exhaust pipes have been stepwise developed from the mid 1970s', thus a sharp distinction can be made between the four main generations up to the mid 1990s. First, from 1976 to 1979, the two-way catalysts, containing Pt and Pd, allow the reduction of HC and CO emission. The second generation, from 1979 to 1986, is the introduction of the so-called “three way catalysts”, including in Pt, Pd, and Rh, which served also to reduce the emission of NO_x . The third type, from 1986 to 1992, a novel generation of three way converters, is still based on Pt and Rh, but better suited to high temperature working conditions, to which the catalysts were exposed with the new, fuel efficient engines. Finally, from 1992 to the mid 1990s, another generation of three way Pd-rich catalysts extensively applied by car manufacturers both in US and in Europe, in the new models to meet the even stricter emission legislation.

Catalytic converters generally have a service life of between 50 000-100 000 miles; however, there are several factors, which can reduce this lifetime. These include in Pb pollution, engine ignition/fueling faults, usage of the vehicle, and short journey use, preventing the converter from reaching the optimal working temperature (around 400 °C). The principal cause of converter failures is carbon pollution, leading to a partial, or sometimes, a total blockage of the catalyst, and the internal fracture of the catalyst surface, usually induced

by external/internal physical damage. Pt, an effective oxidation catalyst for CO and HCs, is unfortunately more sensitive to “catalyst poisoning” than Pd; consequently, it can only be employed in cars fueled with unleaded petrol. In the future, it is very likely that Pd-based catalytic converters become extensively applied, instead of Pt-based ones, due to the lower costs of the former.

PGM emission by catalytic converters

The washcoat, carrier of the “active” precious metals with a diameter in the nanometer range (1-10 nm), contains typically the total amount of 1.5-2.5 g Pt on its surface (Rosner and Hertel, 1986; Zereini et al., 1997a). During the release of the exhaust gases from the engine, the surface of the washcoat is chemically and physically stressed by the fastly changing oxidative/reductive conditions, high temperature and mechanical abrasion, thus, producing the emission of PGM containing particulate into the environment (Rosner and Hertel, 1986; Bärtsch and Schlatter, 1988; Hertel et al., 1990; König et al., 1992; Knobloch et al., 1993; Barefoot, 1997; Artelt et al., 1999a). The amount and rate of PGM emission from the catalytic converter are affected by the speed of the automobile, the type of the engine, the type and age of the catalyst, and the type of fuel additives (Artelt et al., 1999a; Ely et al., 2001). Emission can be intensified by unfavourable operating conditions (misfiring, excessive heating), which may even destroy the converter (Schäfer and Puchelt, 1998).

The quantity of PGMs released into the environment has been evaluated mainly by two methods. The first is the direct determination of PGMs in exhaust fumes, which requires an effective sampling procedure able to collect representative amounts of the released particles. The second involves in the determination of the anthropogenic PGM concentration in environmental materials, such as soils, airborne particles, sludge, water, road dust, etc., and the modelling of the analytical results together with traffic statistics (Moldovan et al., 1999). Direct determination of Pt emission from different (fresh and aged) automotive monolithic catalysts has been performed in run exhaust fumes sampling under laboratory conditions on a computer-controlled dynamometer (König et al., 1992; Artelt et al., 1999a).

The PGM emission rate ranged between 65 to 180 ng km⁻¹ driven depending on whether it was measured in motor experiments, or calculated on the base of environmental

concentrations (Palacios et al., 2000a, 2000b). The same emission range was also observed for various converter models of diverse manufacturers. Rising PGM emission was pointed out with increasing (simulated) car speed, reaching a mean value of approximately 90 ng km^{-1} at 130 km h^{-1} for new converters (König et al., 1992; Artelt et al., 1999a). Under real driving condition, the emission may be even higher than those determined from test stand experiments (Cubelic et al., 1997; Helmers, 1997; Zereini et al., 1997a).

Several dynamometer experiments were performed on various engines to evaluate the PGM emission from the three-way automotive catalytic converters of diverse ages (König et al., 1992; Artelt et al., 1999a). The emitted Pt concentration ranged from 7 to 123 ng m^{-3} ; these values correspond to emission factors of 9 to 124 ng km^{-1} (Artelt et al., 1999a). The converter brands, supplied by various manufacturers, have no significant difference in the Pt-emission. The lower powered engines (1.4 l) emitted four times less Pt than the 1.8 l engines, when comparing the new, aged, and old catalytic converters, no difference was observed in the Pt emission. A lower emission tendency was observed with the increasing age of the converters, which was significant at high-speed conditions, manifested in a five-fold lower Pt emission from old converters, compared to new ones. The Pt emission differed significantly for new converters under various operating conditions. Under constant speed conditions, the Pt emission was usually higher at 130 km h^{-1} compared to 80 km h^{-1} . According to the size distribution of the emitted particles, the large particles ($>10 \text{ }\mu\text{m}$) were dominated (62-67 %), whereas the medium size fraction ($3.1\text{-}10 \text{ }\mu\text{m}$) was about 21 %, and the small ($<3.1 \text{ }\mu\text{m}$) size around 13 %. Generally, the medium age and old converters tested with the 1.8 l engine showed a similar pattern. The soluble and the volatile Pt species were tracked by the application of double-layered glass fiber filters and condensate traps, respectively. It was found that the “soluble Pt” was on average around 1 % of the total Pt emitted, also in the Dimroth-type condenser, whereas no Pt was found in the liquid nitrogen trap (Artelt et al., 1999a).

Most of the PGMs, released from catalytic converters, are in particulate form (Pt $>$ 95 %, Pd $>$ 85 %, and Rh $>$ 90 %) and are dispersed into the environment at a rate of few ng PGM per km per car (König et al., 1992; Moldovan et al., 1999, 2002; see also Table 4). However, some estimates of the PGM concentration in roadside soil approach 270 ng km^{-1} for Pt

(Zereini et al., 2001b). Examination of these particulates showed that around 99 % of Pt is in the metallic state with around 1 % present as oxidized Pt, presumably in the form of Pt⁴⁺ (Schlögl et al., 1987; Artelt et al., 2000). Early experiments also revealed the evolution of some volatile Pt(IV) oxide, when heating Pt metal at 500 °C contacted with air, or oxygen (Balgord, 1973). The particulate Pt exists in the form of surface oxidised metal nanoparticles attached to larger alumina particles (substrate), and hence, the ablated washcoat particles are considered to be the carrier of the precious metals (Rühle et al., 1997). A similar observation on the existence of these “carrier” particles was made by Rauch et al. (2000b; 2002), and also the association of PGMs with Ce (“fingerprint”) originating from the washcoat was concluded. However, the assumption that PGMs are mostly released in metallic form has been challenged by a recent study, based on solubility experiments with roadside PGMs (Jarvis et al., 2001). It was concluded that the PGMs, emitted by the catalytic converters, may not be in metallic form in exhaust fumes, or at least they could rapidly altered, once when they are deposited in the environment. In addition to alumina, silica was also identified as a carrier for the Pd particles of vehicle catalyst origin, probably bound as halogenated compounds (Dongarrá et al., 2002). The particulate, soluble and total PGM content of the exhaust fumes are given in Table 5.

PGM emission from hospitals

Since the first report on the retardation activity of some simple platinum compounds at *E. coli* culture proliferation (Rosenberg et al., 1965), a very extensive and growing application of Pt complexes has been observed as highly effective anti-tumour, or “anti-neoplastic” drugs for treating testicular tumours, ovarian carcinomas, bladder tumours, and tumours of the head and neck (Keppler, 1993). Cisplatin [cis-diaminedichloroplatinum(II)] and carboplatin [diamine(1,1-cyclobutanedicarboxylato) platinum(II)] have been successfully employed for the treatment of human malignancies (Allwood and Wright, 1992). These drugs were introduced more than 25 years ago as antitumour agents, and second generation antitumour platinum complexes are now under medical trial (Keppler, 1993; Kizu et al., 1995). Platinum is excreted by the patients after administration of the anti-neoplastics. As neither hospital sewage, in general, or urine and excretions originating from patients treated with anti-

neoplastics are specially processed, the platinum is released into the hospital sewage, as is also true for other drugs (Kümmerer and Helmers, 1997). These authors concluded that the PGM emission stemming from hospitals is of minor importance to environmental inputs in comparison with other anthropogenic sources, particularly the automotive catalytic converters. For example in Germany, the Pt and Rh content of hospital effluents were reported as 2.2 and $<0.01 \text{ ng l}^{-1}$, respectively (Helmers and Mergel, 1998). Kümmerer and Helmers (1997) found Pt concentrations between 115-125 ng l^{-1} in hospital effluents; these values decreased to 1-2 ng l^{-1} after dilution by communal sewage under dry weather conditions.

The concentration of platinum in the sewage of five European hospitals (in Austria, Belgium, Germany, Italy, and The Netherlands), originating from excreted anti-neoplastic drugs, was analysed to provide reliable data on the Pt emission from hospitals into the aquatic environment. It was shown that 70 % of the Pt, administered in the form of either cisplatin, or carboplatin, is excreted, and, therefore, would end up in hospital effluents. Pt concentrations, measured in the total effluents of hospitals, ranged widely from less than 10 ng l^{-1} (the detection limit of the analytical method) for the Belgian and Italian hospitals to ca. 3500 ng l^{-1} for the Austrian and German hospitals. In all cases, the effluents of the sewage were below 10 ng l^{-1} , as a result of dilution within the waste water system. The highest Pt concentrations in sewage influents were observed at the beginning of rain periods, and at the end of cold periods, when snow was melting. Finally, it was concluded that the main input of Pt into municipal sewage was urban and road run-off from traffic and other Pt emitting sources, and not from hospital sewage (Kümmerer et al., 1999). Annual emissions by hospital and cars in Germany, Austria and The Netherlands are given in Tables 6 and 7. Comparative analysis on the existing emission data of hospitals and traffic related catalysts reveals that, at present, the latter has a considerably greater contribution to the environmental PGM contamination.

PGMs in environmental matrices

A great number of studies have reported the dispersion and accumulation of precious metal in various environmental compartments. Most of the investigations involved in sampling and analysis of soil and vegetation adjacent to heavily travelled highways, and of

road dusts swept from the surface of highways. Measurement of the PGMs requires highly sensitive analytical methodology. Platinum is the element that has received the most attention among the PGMs studies, while Pd and Rh have been monitored in more recent research projects.

PGMs in air, and airborne particulate matter

Analytical difficulties restrict the number of studies dealing with PGM concentration in air and airborne particles. Low PGM concentration in the environmental samples combined with numerous interferences in the most sensitive analytical techniques (Rauch et al., 2000a) are considered to be the major difficulties. In the first report of this particular topic, the Pt concentration in air was reported to be lower than 0.05 pg m^{-3} near a freeway in California (Johnson et al., 1975). However, other studies in Germany have shown that the total Pt concentration in air along a highway ranged from 0.02 to 5.1 pg m^{-3} (0.6 to 130 ng g^{-1}) with the Pt mainly present in the small particle size fraction (from 0.5 to $8 \text{ }\mu\text{m}$), whilst the larger airborne particles had a lower Pt content. The proportion of soluble platinum in air particles varied from 30% to 43% (Alt et al., 1993). A mean Pt concentration of 7.3 pg m^{-3} has been measured inside Munich city buses and tramways during regular rides, with a strong correlation with traffic density (Schierl and Fruhmann, 1996). Petrucci et al. (2000) reported a significant difference for the PGM content of air in urban and remote sites of Rome. The PGM concentration in urban airborne particulate matter ranged at 21.2 - 85.7 pg m^{-3} for Pd, 7.8 - 38.8 pg m^{-3} for Pt, and 2.2 - 5.8 pg m^{-3} for Rh. In Madrid, the Pt and Rh concentrations in airborne particulate matter ranged from 3.1 to 15.5 pg m^{-3} , and from not detectable to 9.32 pg m^{-3} , respectively.

Platinum was not found in the ambient air above the detection limit (0.05 - 1 pg m^{-3}) prior to the use of automobile exhaust converters (König et al., 1992). However, in 1991-1992, a concentration of 0.02 - 5.1 pg m^{-3} of Pt was found in airborne particulate matter (Alt et al., 1993), which increased up to 30 pg m^{-3} near roads. In city buses in Munich, an average Pt concentration of 33 pg m^{-3} was established (Schierl and Fruhmann, 1996). The airborne Pt concentration has shown a significant increase during the sampling period from 1995 to 1996 with the mean of $21.5 \pm 13.8 \text{ pg m}^{-3}$, and the maximum value of 62 pg m^{-3} (Schierl, 2000).

In a recent study, the PM₁₀ (particulate matter with aerodynamic diameter below 10 µm) concentration of PGMs in the urban area of Göteborg was found to be 0.1-10 pg m⁻³ (Pd), 0.9-19 pg m⁻³ (Pt) and 0.3-4 pg m⁻³ (Rh) with higher values for greater traffic intensity. These concentrations provided a general background for the urban atmospheric environment, and the Pt:Rh ratio (4.2) agrees well with the known automobile catalyst composition (Rauch et al., 2001). The PGM concentration in the ambient air of a suburb of Berlin was found to be in the range from 0.2 to 14.6 pg m⁻³ (Tilch et al., 2000). Weather and seasonal conditions did not seem to have a noticeable influence on the PGM concentration in the air. Although the use of Pd catalysts in 1997 was still small compared to Pt and Rh based catalysts, the Pd content of air was similar to that of Pt at the beginning of the 90's.

In Germany, the total Pt, found in airborne particle matter in relation to the total volume of air filtered, was estimated and found rising from an average of 3 pg m⁻³ (in 1988) to 147 pg m⁻³ (in 1998). This represents a 46-fold enhancement over a ten-year period, whereas the Rh concentration increased by 27-fold (Zereini et al., 2001a).

The platinum concentration of the air was monitored in various work places, exhibiting precious metal emission (i.e. Pt mines, Pt refineries, and catalyst manufacturers). In general, the Pt content of air was found to be at the µg m⁻³ level, or below, whilst, in badly ventilated work places, the Pt concentration reached the mg m⁻³ level (Shi, 1998).

The Pt and Rh concentrations of air in Madrid considerably varied with the location of the sampling site (mainly dependent on the traffic density), ranging from <0.1 to 57.1, and <0.2 to 12.2 pg m⁻³ with a median values of 12.8 and 3.3 pg m⁻³, respectively, corresponding to a Pt:Rh ratio of 4 (Gómez et al., 2001). Studies by aerosol collectors (e.g. WRAC and PM₁₀ cascade impactors) allow the evaluation of the Pt distribution in airborne particulate, as a function of the aerodynamic particle diameter from <0.39 to 9 with PM₁₀ collector and from 10 to 65.3 µm with WRAC impactors. Platinum was found in a wide range of the particles of diverse aerodynamic diameter (from <0.39 µm to 65.3 µm). The highest Pt values were found, in most cases, in the particle fraction of the lowest size (<0.39 µm), revealing a rather non-homogeneous distribution of Pt in airborne particulate matter (Gómez et al., 2001, 2002).

Schäfer et al. (1999) drew a distinction between the time-dependent change of PGM concentrations and ratios in various environmental compartments. It was shown that the short-term variation of PGM concentrations and their ratios in road dust were due to wind and rain, whereas the long-term trend reflected the changing proportions of PGMs used for converter manufacturing. At a typical urban site, the daily deposition rate of Pt in airborne dust was up to 23 ng m^{-2} . The integration of these data resulted in an estimate of the total PGM accumulation and the mean emission rates that were found to be significantly higher than those predicted from experimental results of stationary motor experiments. Run-off contributed to the composition of sewage but seemed to be less important, compared to other sources, in the total PGM input into urban sewage sludge. An overview on the PGM content of the airborne samples is listed in Table 8.

PGMs in soil, dust and vegetation

Soil exposed to high traffic densities exceeds the natural background value of PGMs, and is influenced by traffic conditions. Hence, most of the investigations have involved in samples of soil and vegetation adjacent to heavily travelled highways and of road dust swept from the surface of roadways. Data have also shown an upward trend of Pt concentrations with time in these particular environmental matrices. However, for several reports on the roadside vegetation, the data do not necessarily represent the real PGM uptake, but rather the dust deposition, collection and adsorption on the external surfaces of the roadside plants.

Cubelic et al. (1997) found up to 250 ng g^{-1} Pt content in roadside soils down to local background values (below $0.5\text{-}0.8 \text{ ng g}^{-1}$) near German highways. The Pt:Rh ratios were about 6, close to that applied in catalytic converters. Evidence was found for a significant correlation of PGM 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.

Heinrich et al. (1996) analyzed PGM in soil near the Wiesbadener-Kreuz (A3 motorway, Frankfurt-Köln track, Germany). The results showed a considerable enhancement of Pt (up to $330\pm 223 \text{ ng g}^{-1}$), Pd ($6.6\pm 0.19 \text{ ng g}^{-1}$), and Rh ($7.5\pm 0.15 \text{ ng g}^{-1}$). The content of the rest PGMs (Ir, Os, Ru) in soil was either below the detection limit (Os, Ru), or statistically

spread around the corresponding blank values (0.08 ng g^{-1} for Ir and 0.11 ng g^{-1} for Ru) of the reference soil. It was also observed that the PGM contamination of the soil rapidly decreased with increasing distance from the highway.

Hodge and Stallard (1986) analyzed dust collected from the leaves of roadside plants and found extremely high concentrations, 0.7 and 0.3 ppm for Pt and Pd, respectively. The Pt:Pd ratio was 2.5, which agreed well with the ratio in catalysts of the type applied before the sampling period. The highest concentration of both metals was found in dust collected from plants growing at the edge of streets and highways with heavy traffic, whereas the lowest content was found in grass samples, taken from the streets with light traffic. It was concluded that the dust accumulating along freeways and busy streets could concentrate upwards to 1 ppm Pt and half as much Pd. It was deduced that the first rain after a long dry weather period, common in South California, would accumulate Pt and Pd from rooftops and streets in relatively large amounts of both soluble and insoluble forms, and transport them to the Pacific Ocean (Hodge and Stallard, 1986).

A comparison of Pt concentrations in size-fractionated road dust collected in 1984 and 1991 showed an average increase in all fractions; particles below $63 \mu\text{m}$ size: $3.0\text{-}8.9 \text{ ng g}^{-1}$; $63\text{-}125 \mu\text{m}$ size: $1.5\text{-}3.6 \text{ ng g}^{-1}$; and the $125\text{-}1000 \mu\text{m}$ particle size, $<0.5\text{-}2.8 \text{ ng g}^{-1}$ (Wei and Morrison, 1994a). The surface loadings of Pt were calculated for a car park (26 ng m^{-2}) and a kerbside ($1.28 \mu\text{g m}^{-2}$), and the mean Pt concentrations in highway run-off were calculated to be $0.1\text{-}0.7 \text{ ng l}^{-1}$.

The PGM content of soil and grass, gathered from the USA roadsides, was evaluated by Ely et al. (2001). A Pt abundance of $64\text{-}73 \text{ ng g}^{-1}$ was found immediately adjacent to the roadside, and the corresponding Pd and Rh abundance values were found statistically above the background soil values. Platinum, Pd, and Rh showed positive correlation with traffic-related elements (Ni, Cu, Zn, and Pb), but no correlation with the other trace elements present in the samples (Ely et al., 2001). Similar results have also been reported for the heavily polluted Mexico City (Morton et al., 2001). The contamination of the soil 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. The highest concentration of Pt, Pd, and Rh in the analyzed samples were 300 , 70 and 40 ng g^{-1} , respectively.

Schäfer and Puchelt (1998) analyzed the PGM content in soil and road dust from several sites in Southwest Germany, selected on the basis of traffic density and morphology, including in roads in Stuttgart with 120 000 vehicles per day, and near Heidelberg with 100 000 vehicles per day. At these two monitoring locations, 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 ($\leq 1 \text{ ng g}^{-1}$) at less than 20 m from the road. Maximum Pt and Rh values were reported as 10 and 35 ng g^{-1} , respectively. The PGM concentration decreased significantly in soil samples taken from deeper layers. Lateral and vertical distribution patterns for Pd, Pt and Rh were very similar to those observed by Eckhardt and Schäfer (1997). The Pt, Rh, and Pd contents of road dust ranged up to 1000 ng g^{-1} , 110 ng g^{-1} and 100 ng g^{-1} , respectively, which is an indication of a short-term input of PGMs (Schäfer et al., 1996). They also reported a Pt:Rh ratio of around 6:1 in traffic influenced soil and dust. Dust samples collected in the tunnel of 'Mittlerer Ring' in Munich, Germany, showed an increase in Pd concentrations from $21.8 \pm 3.5 \text{ ng g}^{-1}$ in 1994 to $100.5 \pm 15.1 \text{ ng g}^{-1}$ in 1997-98 (Schuster et al., 2000). This increase is much higher than the growth of the traffic density in the same period of time. Schramel et al. (1995) analyzed road dust collected from the ceiling of an Austrian tunnel, and found Pt concentration of 68.2 ng g^{-1} . It was calculated that for Germany, in the period up to the year 2018, a total of 2100 kg of Pt will be emitted by catalytic converter equipped vehicles, and moreover, the annual atmospheric Pt deposition will be up to $0.73\text{-}4.4 \text{ } \mu\text{g m}^{-2}$, or 260 kg Pt yr^{-1} (vs approximately 100 kg Pt yr^{-1} for the mid 1990s) (Helmerts and Kümmerer, 1999).

The PGM concentration in road dust and surface soils was analyzed near high traffic sites in the United Kingdom (Farago et al., 1996). The Pt concentration ranged from 0.42 to 29.8 ng g^{-1} in road dust, and from <0.3 to 8 ng g^{-1} in soils, while the local background value for soil was 1 ng g^{-1} . The Pt concentration in road dust was highest at major road intersections, ranging from 11.2 to 23.7 ng g^{-1} (mean: 20.8 ng g^{-1}), compared with areas along minor roads (range: 0.35-4.26 ng g^{-1} , mean: 2.29 ng g^{-1}), which again confirmed the positive correlation of the Pt concentration with high traffic density.

Higney et al. (2002) reported significantly raising concentrations of Pt and Pd in road dust and roadside soil in West Central Scotland. The highest Pt concentrations (within the 13-335 ng g^{-1} range) was observed for road dust samples taken at dual carriageways and

motorways, representing a considerable increase relative to surface soils in this area that are remote from roads, which have Pt concentrations of less than 1.0 ng g^{-1} . In contrast, they observed lower Pt levels ($1.8\text{-}11.8 \text{ ng g}^{-1}$) in dust samples taken from a residential area (East Kilbride town). A significant variation of the Pt concentration in road dust was observed at various locations along a trunk road in areas of similar traffic frequency, with the highest values found in roundabout samples. These results suggest that the fluctuation in the concentration of PGMs is directly linked to the traffic conditions, at least nearby the roads.

Rauch et al. (2000) reported increasing concentrations of Rh, Pd and Pt by analyzing two diverse fractions (below and above $63 \mu\text{m}$ particle size) of road sediments taken in Göteborg city. For the 1984 and 1998 years, the PGM content in the fraction below $63 \mu\text{m}$ particle size was found to be significantly increased from 2.82 to 60.4 ng g^{-1} for Rh, from 377 to 472 ng g^{-1} for Pd, from a non-detectable amount to 157 ng g^{-1} for Pt. A very similar trend was observed for the larger particle size fraction.

Gómez et al. (2001) found Pt and Rh content of road dust collected at six sites of Madrid in the $31\text{-}2252$ and $11\text{-}182 \text{ ng g}^{-1}$ range, with an average of 317 and 74 ng g^{-1} , respectively. The average of the Pt:Rh concentration ratio was 4.3 in road dust, a very similar value to that of found in airborne particulate matter (4.0).

Helmerts and Mergel (1998) observed an enhanced Pt and Ph content in grass samples by a factor of 2.7 , and in dust samples by a factor of 3.9 , comparing samples from 1994 and 1997. On the other hand, the percentage of the cars equipped with catalytic converters was 2.4 times higher in 1997 compared with 1994.

Tree bark is an effective substrate for accumulation of atmospheric aerosols and airborne particulate matter; it has been used as a passive bio-monitor for atmospheric pollutants (Walkenhorst et al., 1993). Employing this advantage, Becker et al. (2000) analyzed 57 tree bark samples of sycamore, beech, poplar and horse chestnut, which were collected from rural areas, cities (Sheffield, London), and from sites adjacent to industrial activity. The Pt content of the sampled bark ranged from 0.07 to 5.4 ng g^{-1} . The concentration of Pt in uncontaminated tree barks ($<0.01 \text{ ng g}^{-1}$) and contaminated samples (up to several ng g^{-1}) were of similar magnitude as the Pt contamination in grass samples from rural areas

i.e. 0.1-0.3 ng g⁻¹ (Angerer and Schaller, 1994; Merian, 1991), and from the areas exposed to traffic: 0.8-3.0 ng g⁻¹ (Alt et al., 1997; Helmers et al., 1994).

Ma et al. (2001) collected 77 samples of tree bark from the following areas: Sheffield and London (UK, 28 samples), Madrid and Tenerife (Spain, 13 samples), Tokyo and Yahushima (Japan, 26 samples) and San Francisco and Hawaii (USA, 10 samples). Platinum concentrations found in the remote sites were below 9 ng g⁻¹; similar concentrations were obtained for Spanish/UK cities with occasionally slightly elevated values. In contrast, the concentration for bark samples in major Japanese/US cities ranged up to 38 ng g⁻¹; the data are consistent with the use of Pt-fitted automotive catalysts in the respective sites.

Dongarrá et al. (2002) examined the occurrence of Pd and Pt in pine needles (*Pinus pinea* L.) collected in and around Palermo city, Italy. The observed PGM concentrations ranged from 1 to 102 ng g⁻¹ for Pt, and from 1 to 45 ng g⁻¹ for Pd, higher by two orders of magnitude than the crustal abundance, suggesting a common antropogenic source, the vehicle catalyst. The distributions of PGMs were found highly non-homogeneous, which revealed a similar distribution pattern in airborne particles.

Platinum and Pd concentrations in garden soil and road dust were analyzed in samples taken from the Nottingham city (UK) in 1996 and 1998, and compared with the archived samples taken in 1982 (Hutchinson et al., 2000). A significant increase in road dust was found, with Pt and Pd values ranging up to 298 and 556 ng g⁻¹, respectively, in 1998 (see Table 9).

From the above studies, in general, we can conclude that the PGM concentrations do significantly depend on the vehicular density and the concentration of these metals increases continuously near roadways. The distribution of PGMs in soils nearby roads, is not only affected by the turbulence of vehicles passing along the roads, but the prevailing wind direction as well (Schäfer and Puchelt, 1998). The results of soil and roadside dust analyzed for PGMs are shown in Table 10, whilst the PGM concentrations in the vegetation are listed in Table 11. The interaction of diverse PGM species with soils is discussed in detail in the section “Transformation of PGMs”, whilst the PGM uptake by various sorts of plants is exposed in the section “Bioaccumulation and Bioavailability of PGMs”.

In addition to localized studies in urban and rural areas, Barbante and co-workers (1999, 2001) found that Pt concentrations in remote snow cores from Greenland and in the Alps have been considerably rising since 1975, and had increased up to 40-fold (median values from 0.01 to 0.33 pg g^{-1}) up to the mid-1990s. In snow samples, the concentrations ranged from 0.0008-2.7 pg g^{-1} for Pt, 0.01-16.9 pg g^{-1} for Pd, 0.0005-0.39 pg.g^{-1} Rh. The Pt:Rh ratio was found to be very close to that of in catalytic converters. The fact that these PGM polluted places are located at high altitudes and far away from residential areas, indicates a large-scale contamination impact of the vehicle catalysts, likely through the troposphere of the Northern Hemisphere. Moreover, Van de Velde et al. (2000) observed increased concentrations of Pd, and Rh in the Mont Blanc ice and snow samples, especially for the last decade, whilst no clear enhancement was found for Pt. The PGM content of these samples was in the range of 0.08-0.62, 0.5-10, and 0.01-0.39 pg g^{-1} for Pt, Pd, and Rh, respectively.

PGMs in rivers, coastal waters and oceans (in the water ecosystem)

Several studies have given an account on the increasing PGM concentration in various parts of the water ecosystem, i.e. rain-, drinking-, ground-, and seawater; river and oceanic sediments, sewage sludge, etc. (see details in Table 12). The PGM enrichment in these matrices can mostly be linked to release from automotive catalysts and evidence for post-depositional mobility of Pt and Pd in contaminated sediments.

Early studies on Pacific seawaters, dating back to the 1980's, reported very low levels of Pd and Pt, 40 and 150 pg l^{-1} , respectively (Lee, 1983; Goldberg et al., 1986). On the other hand, an enhanced Pd concentration was observed in freshly deposited coastal sediments in the moat that surrounds the Emperor's Palace in Tokyo (Lee, 1983). This local Pd gradient was attributed to the run-off from adjacent roads of frequent automobile traffic, and as a consequence of the Pd emission stemming from the use of catalytic converters.

Hodge et al. (1986) analyzed more than 100 samples of seawater, sediments, algae and manganese nodules for Pt and Ir. Platinum was determined in seawater samples collected at the Californian coast, which showed a concentration rise from 100 pg l^{-1} at the surface water to about 250 pg l^{-1} at 4500 m depth. The Pt values in macro algae, ocean sediments and

manganese nodules ranged from roughly 0.1 ppb in algae to around 1 ppm in the nodules. Manganese nodules at shallow depth have been reported to have the highest Pt content in the oceanic environment (Hodge et al., 1985). Iridium values ranged from 9×10^{-4} ppt for seawater to 7.4 ppb for manganese nodules. The Pt concentration in 24 oceanic sediments was found to be on average 0.0038 ppm (Goldberg et al., 1986), very close to the estimated crustal abundance.

The concentration of Pd in water from the Rhein and Schwarzbach rivers (Germany) was estimated at 0.4 ± 0.1 ng l⁻¹ (Eller et al., 1989), which value is well below those found in ground and rainwater. Hall and Pelchat (1993) determined Pt and Pd in fresh-water samples collected from some mineralized sites of Canada; dispersion patterns could be identified, but maximum concentrations of these elements (soluble part) were below 5 ng l⁻¹.

De Vos et al. (2002) surveyed the distribution of all the PGMs in the contemporary sediments of Kentish Stour (UK). The highest abundances occurred in the motorway run-off sediments (maximum total PGM content of 50 ng g⁻¹), while the lowest values were recorded in sedimentary rocks. The total PGM content of the river sediment ranged from 0.4 to 10.8 ng g⁻¹. The authors concluded that the PGM distribution in the sediments corresponded strongly with land-use changes (urban versus rural sections) and with the points of discharge from sewage treatment plants, but no clear single source signature could be identified, such as catalytic converters. This is probably due the contribution of other anthropogenic sources (hospitals, industrial activities) to the PGM content of the river sediments, which, consequently, cause a shift in their concentration ratios.

The Pt and Pd concentration in the sediments of Boston Harbor increased approximately five times compared to the background concentration in Massachusetts Bay as an uncontaminated site (Tuit et al., 2000). Comparative analysis of the archived surface sediments from 1993 and 1996 revealed a 17- and 50-fold enhancement of Pt and Pd concentrations, respectively, compared to the PGM level in 1978. These levels do not exceed that found in Mn nodules in the deep sea (Hodge et al., 1985, 1986). Rauch et al. (2000) analyzed the sediments of the Mölndal river in Göteborg, Sweden, and found 0.67, 13.9, and 1.0 ng g⁻¹ of Rh, Pd and Pt, respectively. Although these concentrations are relatively lower

than found in other environmental matrices, a larger impact can always be expected on aquatic life through bio-accumulation.

The concentrations of Pt and Pd in sewage sludge and effluent particles from Boston city were measured to estimate the magnitude of the 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. The concentration values found for the Boston sludge are similar to those of reported in the sludge from New York, and additionally, to those reported for the sludge of 24 German cities (Lottermoser, 1994). The authors implied that the PGM enrichment is ubiquitous through industrialized areas. On the other hand, the higher Pd content of the sludge samples compared to Pt, suggested an additional anthropogenic source of this element and/or Pd is more particle reactive than Pt. Laschka and Nachtwey (1997) tracked the Pt concentration in sewage and sludge of two large sewage treatment plants during dry and rainy weather periods. The Pt concentration and load increased in primary effluents, which were influenced by rainfall compared to dry weather conditions. Daily Pt loads indicated, however, that in a large industrial area, such as Munich, the traffic is likely not the dominant source of Pt in municipal sewage. Comparative analysis of sewage sludge from 15 plants in smaller rural towns shows that the Pt concentration in sewage sludge of Munich was considerably higher. In a recent work, Helmers et al. (1998) explained the increased Pd content in sludge from Stuttgart with the enhanced emission of the German dental industry. Other possibilities are the electroplating waste associated with jewelry and electrical industries, and most importantly, the chemical industries, which can release dissolved, and/or readily dissolvable compounds of PGMs (Tuit et al., 2000).

Transformation of PGMs in the environment

From the above literature survey, it is clear that the PGM concentration is increasing significantly in the environment. Hence, it is important to study the mobility of these metals under the sometimes very rapidly changing environmental conditions. Most of the PGMs are referred to as behaving in an inert manner, and to be immobile (Zereini et al., 2001b). However, it is important to study how these metals may become chemically/biochemically

active, and mobile in interactions with different environmental matrices under changing weather conditions, in order to follow the possible hazard for human health.

Zereini et al. (1997a) crushed a catalytic converter (monolith) and milled it to a particle size of less than 63 μm to study the geochemical behaviour of PGMs (i.e. to assess their mobility via species transformation). Soil was contacted with the above model material, and after varying the conditions, such as pH, Cl^- , or S concentration, the solubility of Pt and Rh was determined. The results from these model experiments were compared with those from various environmental materials (soil, run-off sediments, surface water, tunnel dust). The environmental materials exhibited a relatively constant Pt/Rh ratio of 5, which points to a common anthropogenic source, the automobile catalyst. The highest solubility of Pt and Rh was established in rainwater at pH=1, giving a maximum total solubility of 0.35-0.5 % Pt and of 1.0 % Rh for the catalytic material introduced. Under natural conditions in roadside soils, only pH values between 5 and 8 are relevant. However, within this pH interval, the total solubility is considerably lower, and nearly constant: 0.01-0.025 % for Pt and 0.05 % for Rh. The relative solubility of Rh was found to be higher than that of Pt, and the Pt:Rh ratio fluctuated between 1 and 4.

The increasing NaCl concentration applied in soil samples does not have any recognizable effect on the solubility of Pt and Rh (Zereini et al., 1997a). This result indicates that no seasonal change on the solubility of Pt and Rh should occur in nature; the maximum solubility is 0.03 % and 0.6 %, for Pt and Rh, respectively. Increasing the S concentration in soil positively affected the solubility of Pt, whereas that of Rh remained unaltered (Zereini et al., 1997a). The total Rh solubility remained at 0.05-0.06 %, while Pt had a maximum value of 0.03 %. It was also shown that even rainwater was capable of dissolving colloidal Pt and Rh. However, the latter was experienced with used catalysts, and hence, it is possible that small amounts of Pt and Rh chloride salts (as residues from the manufacturing process, usually in negligible quantity) were dissolved. Nachtigall et al. (1996) observed a low Pt solubility in deionized water, which significantly increased on the addition of certain anions to water. The portion of soluble Pt was found to be dependent on the particle size distribution, and also, only a certain fraction was immobilizable (dissolvable) from the surface of alumina particles (carrier).

Alt et al. (1993) demonstrated that even 2.5-6.9 % of the total PGMs present in traffic-related dust was soluble. Hill and Mayer (1977) found 10 % to be soluble in samples of a similar type. Lustig et al. (1996) found that 3.9 % of the total Pt was water soluble in tunnel dust samples, whereas no significant dissolution was observed in most of the organic solvents (dichloromethane, hexane), but 3.11 % of the total Pt was received in the methanolic fraction. These experiments proved the importance of using real samples (e.g. tunnel dust), instead of model materials for the dissolution studies. Direct analysis of car exhaust fumes revealed that less than 10 % of the total evolved PGM particulate for new catalysts is soluble, whereas this fraction was higher for aged catalysts, especially, for Rh and Pd (Moldovan et al., 2002).

Rainwater usually provides a significant medium for the transportation of PGM particles until deposition. In run-off water up to $1 \mu\text{g l}^{-1}$ Pt was found (Helmers et al., 1994; Laschka et al., 1996). The sample from the sediment cores of a drainage basin (Frankfurt) reflected a low mobility and slight solubility of PGMs (Zereini and Alt, 1999). Traffic-related metals (Cr, Ni, Cu, Zn, Cd, Pb, As, Rb and Ba) were also concentrated in the upper 20-25 cm layer (Golwer and Zereini, 1998).

Similarly to soil samples (Rankenburg et al., 1995; Zereini et al., 1997b), the Pt:Rh ratio in run-off reservoir sediments remained relatively constant (4.6), and a strong correlation was found between Pt and Rh. These results are indicative for a common source, the catalytic converter, during the time interval 1987-1995 (correlated with 0-25 cm depth). Surface water samples from run-off reservoirs along different highways gave the same coherence. Zereini et al. (1997b) reported the presence of only small amounts ($9-78 \text{ ng l}^{-1}$) of Pt in water samples at $\text{pH}=5.8-6.7$. No consistent trends have been found in individual basins, or among their groups, and additionally, the data scattered to a great extent. Dependency on the traffic flow, area of occupation, water quantity, and the residence time may affect these values. These results are in accordance with those of reported by Fuchs and Rose (1974), who investigated the geochemical behaviour of Pt in soil in the vicinity of the Stillwater Complex (Montana, USA), at a major Pd/Rh ore deposit. Platinum showed considerable mobility, only in extremely acidic, and chloride-rich soils, possibly as a consequence of complex formation of the divalent Pt yielding $[\text{PtCl}_4]^{2-}$. These findings may eventually have an influence on the drinking water quality. Laschka and Nachtwey (1993) found Pt in drinking water below 0.1

ng l⁻¹, whereas groundwater exhibited values of 3-38 ng l⁻¹, and rainwater yielded values of 1.4-74.5 ng l⁻¹.

Hodge et al. (1986) pointed out that marine waters from the Pacific Ocean contained 0.23 ng l⁻¹ Pt, whereas Messerschmidt and coworkers (1992b) found 2.2 ng l⁻¹ Pt in shallow waters of the Baltic Sea. By taking into account the increasing density of civilization and the industrial areas around the sampling area, this ten-fold enrichment may be interpreted as an anthropogenic impact.

In Sweden, the particle fraction below 63 µm in the roadside dust samples contained 39-88 % less Pt than the gully pot sediments with a Pt content from 3.5 to 15 ng g⁻¹ (Wei and Morrison, 1994b). Sequential extraction of Pt from road surface sediments showed that Pt appeared in the following operationally determined fractions: exchangeable, 15 %; carbonate, 10 %; Fe/Mn, 32 %; organic, 26 %; and residue, 26 %. In gully pot sediments, Pt was found only in organic form. Consequently, a transformation mechanism of Pt was offered, based on the interaction of inorganic Pt with the high organic content of gully pot sediments (Wei and Morrison, 1994b). The interaction of metallic Pt with micro-organisms in humic soil was found negligible, thus a chemical dissolution route was justified (Lustig et al., 1997c).

Inorganic mineral phases, particularly in the clay fraction, as well as organic soil materials, like humic substances, can adsorb heavy metals (Herms and Brümmer, 1978). However, their behaviour in connection to PGMs is not well established. Some experimental data on the montmorillonites (Skerstupp et al., 1996), and synthetic ferrihydrite (Skerstupp et al., 1995) illustrate PGM enrichment at these phases, most obviously in the case of ferrihydrite. The behaviour of Pt compounds in soil is reported to be dependent on chemical (oxidation state, complexation; Lustig et al., 1996) and physical (colloidal particle size; Nachtigall et al., 1996) characteristics.

Lustig et al. (1998a) studied the interactions between various Pt species (PtCl₄²⁻, PtCl₆²⁻, Pt powder, or tunnel dust with 0.02 µM Pt) and soil/humic acid using diverse reaction times (3, 7, 14, 30 and 60 days). The Pt containing aqueous fraction, “extract”, was taken and analyzed. It was found that the total amount of PtCl₄²⁻, PtCl₆²⁻, was converted into the extract, whereas in the extract of the “native sample”, i.e. tunnel dust with Pt, the presence of apolar Pt species was found. The same trend was observed when Pt powder was tested with humic

acid, which indicates the presence of many species transformation in these particular matrices. These results indicate well the very efficient transformation of some Pt species in connection with soils, in a relatively short time. These findings do not agree with the results of previous works (Zereini et al., 1997a), which state the slight solubility of the Pt species released by the catalytic converters.

In other works, several natural complexing agents (adenosine, ADP, ATP, L-histidine, humic acid fraction, L-methionine, pyrophosphate, and triphosphate) were treated with metallic platinum (as Pt black and as a Pt(0) containing tunnel dust) for 3-60 days. Some of the compounds used could dissolve Pt(0) to a recognizable degree, whereas others were in the range of the aqueous blanks. Comparison of Pt black with a natural dust sample showed that L-methionine had in both cases the greatest effect after 60 days. Generally, more Pt(0) was dissolved in the dust sample (finer dispersion and smaller particle size) than in the Pt-black used. By carrying out the experiment under natural conditions instead of in pure oxygen, the amounts of dissolved platinum are about one order of magnitude lower (Lustig et al., 1998b).

Automobile exhaust catalytic converters emit mainly finely dispersed metallic Pt in the nanometer size range deposited on the layer of aluminium oxide carrier particles. PGMs in catalysts form finely dispersed particles in the nm-range. Although the PGMs in these “metallic islands” have a formal oxidation state of zero, their colloidal, or rather “cluster” state is also meta-stable, and thus, provides a more ready access for chemical reaction than the bulk metal.

Furthermore, in a recent work, a considerable increase in the Pt, Pd and Rh concentrations, by factors of 40, 80, and 120, respectively, has been observed by sampling from the remote Greenland snow-cores in the mid 1990, compared to ancient ice dating back from B.C. 5000 (Barbante et al., 1999, 2001). These results show that the spread of PGMs in the environment is rather a global process, despite some works asserting the low transportability of these pollutants.

It can be concluded from the above overview that despite the generally accepted fact that PGM emission takes place in metallic, or oxide forms (König et al., 1992), there is experimental evidence that at least part of the evolved particles is soluble, and can undergo a transformation in contact with various kinds of compounds in the environment, thus,

providing PGM compounds ready to enter into the food chain. Nevertheless, the existing literature data is in some issues somehow contradicting, and much attention should be paid to the speciation studies of PGMs in environmental matrices to assess more reliably the transformation of the anthropogenically evolved PGM in the nature.

Bioaccumulation and bioavailability of PGMs

The increasing use of PGMs in catalysts together with other application has resulted in the spread and bioaccumulation of these species in the environment. Pd, Pt and Rh in the catalyst dust are deposited along roadways, on adjacent vegetation and soil, and in water bodies either directly, or through run-off (Wei and Morrison, 1994a).

Very little is known about a possible uptake of the traffic related PGMs by the terrestrial biosphere. Elevated and continuously increasing Pt and Pd concentrations were described in field studies for roadside grass samples (Helmers and Mergel, 1997; Hees et al., 1998; Laschka et al., 1999; Schuster et al., 2000). In greenhouse experiments, various plant species like spinach (*Spinacia oleracea* L.), cress (*Lepidium sativum* L.), stinging nettle (*Urtica dioica* L.), and phacelia (*Phacelia tanacetifolia*, *Angelia*) were grown in soils containing PGMs (Schäfer et al., 1998). Sauerbeck (1989) defined the transfer coefficient as the ratio of the concentration in plant and the concentration of the element in soil. Following this concept by Schäfer and co-workers (1998), the transfer coefficients of Pt, Rh and Pd were found to be within the range from immobile to moderately mobile elements. The transfer coefficients decreased in the order of Pd>Pt≥Rh; consequently, it can be concluded that Pd is the most biologically available of this group.

In some model experiments, a standardized culture of grass (*Lolium multiflorum*) was exposed at heavy and light traffic locations with diverse PGM emission intensity (Rosner et al., 1991; Wäber et al., 1996). The Pt content of the grass ranged from 0.8 to 2.9 ng g⁻¹ at the exposed sites, and from 0.2 to 0.5 ng g⁻¹ at locations with less exposure in 1992 and 1993 (Wäber et al., 1996). However, the increased concentration of PGMs was due to the deposition on the plant surfaces rather than on the real uptake.

The first attempts to isolate Pt species from grass were focused on the high molecular weight range (>10 kDa) by Messerschmidt et al. (1994, 1995). For “native” grass (not treated

with Pt), they isolated one main Pt-binding protein with 180-195 kDa. In grass, treated with Pt (uptake exclusively by the roots), this fraction of high molecular weight species increased and seven additional species were detected in the 19-1000 kDa range. In contrast to the native grass, however, most of the adsorbed Pt (>90 %) was found in the low molecular weight range (Messerschmidt et al., 1994). The study of low molecular weight species (<1500 Da) in grass revealed that the Pt binding ligands can be characterized as partly oxidized oligosaccharides (about 2-5 monomeric units of aldonic, aldaric, or uronic acids). The origin of these species was attributed to the hydrolysis of biopolymers, such as pectin (polygalacturonic acid) (Alt et al., 1998).

Lustig et al. (1997a, 1997b) also gave a proof of the platinum uptake under natural conditions by some nutrient plants, i.e.: onion (*Allium cepa* L.), radish (*Raphanus sativus* L.), broad bean (*Vicia faba* L.), Maize (*Zea mays* L.) and Potato (*Solanum tuberosum* L.). For assessing the mass balance of Pt, all possible transport routes into and out of these plant-systems were monitored during the growing period. Plants grown in untreated soil took up less than 1 % of Pt, naturally present in the soil ($0.15 \pm 0.11 \text{ ng g}^{-1}$), whereas the plants grown in Pt-treated soil (in the form of tunnel dust) took up slightly more Pt. The examined onion and radish did not take up Pt to a higher degree in their tubercules. This observation for radish is in contradiction with the results of previous experiments (Pallas and Jones, 1978), which were performed on a cultivation substrate of a high Pt content, generally, from which a higher Pt uptake could be expected.

Klueppel et al. (1998) studied platinum metabolites in cultivated grass treated with aqueous platinum solutions, and also, in model studies, the binding capabilities of methionine, cysteine and glutathione to Pt. The size-exclusion chromatographic analysis of the low molecular mass components (<10 kDa) revealed five well-distinguishable Pt fractions. The binding properties of Pt could be drawn from the multi-element monitoring of some possible partners (C, S, Ca, Pb). It was also concluded that the major part of Pt taken up was not metabolized, but deposited, or stored in the phloem and xylem of the plant, or precipitated in the vacuoles. Most of the Pt was found to being accumulated in the roots of the plants, which is in an agreement with the observations of Ballach (1995) and Ballach and Wittig (1996) on poplar cuttings.

The platinum uptake of rye grass (*Lolium perenne*) cultivated on a sandy loam soil, and cucumber (*Cucumis sativus*) plants grown hydroponically (i.e. without the use of soil) were studied by the assistance of the aqueous solution of the $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$ (nutrient) in the range of $0.5\text{-}50 \mu\text{g l}^{-1}$ Pt (Verstraete et al., 1998). The accumulation factor (AF) was defined as the ratio of Pt concentration in the plant to that in the soil, or the nutrient solution. The grass grown on spiked soil accumulated Pt only to a slight degree (AF: 0.008-0.032). However, the hydroponically grown cucumber plants strongly accumulated platinum (AF ranged from 11 to 42 for shoot, and 1700 to 2100 for the roots). The authors explained the large deviation in the AF values found for shoot and roots by three possible causes: (i) Cucumbers are *dicotyledons*, whereas grass is a *monocotyledon*. The general experience is that *dicotyledons* have higher accumulation ability to metals, compared to *monocotyledons*. (ii) The cucumber plants were exposed to a higher Pt impact than grass cultivates. (iii) The immobilization of the Pt compound occurred in soil.

It can be concluded from the above studies that in “native” cultures, Pt appears to be bound to high molecular mass species (i.e. proteins), whereas in treated (model) cultures a variety of Pt species at the low molecular fraction dominate.

After anthropogenic emission, Pd, Pt and Rh, as well as other heavy metals, can accumulate in fresh water and estuarine sediments and their effects on aquatic life depend on their biological availability. Aquatic macro invertebrates form an integral part of the diet of freshwater fish and can be considered an important step in food chain. Moldovan et al. (2001) examined the bioavailability of Pd, Pt and Rh by the freshwater isopod, *Asellus aquaticus*, both in a natural ecosystem (collected from the Mölndal river in Göteborg) and under laboratory conditions. The isopod showed a Pd, Pt and Rh content of 155 ± 73 , 38 ± 35 , and $18\pm 12 \text{ ng g}^{-1}$ (dry weight), respectively. The exposure of *Asellus aquaticus* to PGM standard solutions for a period of 24 hours yielded a bioaccumulation factor of 150, 85, and 7 for Pd, Pt and Rh, respectively. Exposure of the isopod to environmental samples over various exposure periods demonstrated a time-dependent bioaccumulation, and a higher accumulation from matrices of higher PGM content.

The toxicity of Pt to aquatic life has been studied for several freshwater invertebrates, including *Daphnia magna* (Biesinger and Christensen, 1972), *Lumbriculus variegatus* (Veltz

et al., 1996), and *Asellus aquaticus* (Rauch and Morrison, 1999). The effects of Pd and Rh on aquatic life are not well known.

Several studies on the uptake of traffic emitted PGMs by animals demonstrated a bioavailability of Pt; i.e. for earthworms (Schäfer et al., 1998), rats (Artelt et al., 1999b), and European eels (Sures et al., 2001). Uptake of traffic related Pd by European eels (*Anguilla anguilla*) resulted in a mean liver Pd content of 0.18 ± 0.05 ng g⁻¹ (wet weight). Analysis on the feathers of three raptor species in Sweden have revealed a clear temporal increase of Pd, Pt, and Rh content from 1917 to 1999 (Jensen et al., 2002). Significantly enhanced Rh content was found in peregrin falcon (*Falco peregrinus*) and sparrowhawk (*Accipiter nisus*) feathers, which dated from later than 1986. For this period, the mean Pt, Pd, and Rh content in the feathers ranged from 0.3 to 1.8 ng g⁻¹, 0.6 to 2.1 ng g⁻¹ and 0.1 to 0.6 ng g⁻¹, respectively. The prey of the raptors, i.e. house sparrows (*Passer domesticus*), in urban areas had a considerably higher Pt and Pd concentrations than the urban sparrowhawks. This PGM contamination of the feathers was found to be external, consisting of nanometer-sized particles, and additionally, the Pt and Pd concentrations were significantly higher in the vane than in the shaft of the feathers. The higher Pd concentration, comparing to Pt and Rh, may be a sign of a greater mobility of Pd in the environment, possibly through airborne particles. Although a higher PGM content was found in the feathers of birds living at urban areas, no significant spatial pattern could be established, partly because of the widespread distribution of cars, and partly the birds forage and integrate PGM exposure over large areas (Jensen et al., 2002).

In addition to the availability of PGMs in terrestrial ecosystem, these metals were also introduced passively in aquatic biotopes, e.g. by road run-off (Laschka et al., 1996). Biomethylation of dissolved Pt compounds by bacteria (Brubaker et al., 1975; Peterson and Minski, 1985; Wei and Morrison, 1994b), and biaccumulation of Pt in urban river sediments should be also a possible route to produce bioavailable Pt species (Peterson and Minski, 1985; Wei and Morrison, 1994b).

The only information on the uptake of PGM has been derived from experiments with a high dose of well-soluble salts. The uptake and accumulation effects of PGMs could be advantageously studied on water hyacinth (*Eichhornia crassipes*), because of its remarkable ability to assimilate high levels of transition metals from solutions (Farago and Parsons,

1983). Water hyacinth was capable of recovering PGMs even from dilute solutions to a varying degree, depending on the complex forming ability of the metal, according to the queue of $\text{Pt}^{2+} > \text{Pd}^{2+} > \text{Os}^{4+} \approx \text{Ru}^{3+} > \text{Ir}^{3+} \approx \text{Rh}^{3+}$ (decreasing % recovery at the 0.05 ppm level). The same queue of decreasing relative toxicity was observed for PGMs at the 10 ppm level. The most prominent toxic symptom, even at low Pt^{2+} levels, was the appearance of reddish-brown streaks in the leaves. In contrast to the toxic effect of Pt^{2+} , on the addition of 10 ppm Rh^{3+} , applied as $\text{Na}_3[\text{RhCl}_6]$, water hyacinth increased its biomass some 6.7 % more than the control plants. When the South African grass (*Setaria verticillata*) was treated with 0.5 ppm Pt^{2+} (as K_2PtCl_4), the vascular discolouration was absent, and the roots were stimulated to grow some 65 % more compared to control plants. It was concluded that the toxic effects of Pt substantially depend on the sort of plant species treated. In exposure studies of the same plant, using 0.05-0.10 $\mu\text{g l}^{-1}$ solutions of various Pt, Pd, and Rh salts, the highest accumulation of these noble metals were found in the roots of *Eichhornia crassipes* (Farago and Parsons, 1994). Relative toxicity order, determined from visual appraisal and in terms of oxidation states, was $\text{Pt}^{2+}, \text{Pd}^{2+} > \text{Ru}^{3+} \approx \text{Ru}^{2+} \approx \text{Ir}^{3+} > \text{Pt}^{4+} \approx \text{Os}^{4+} \gg \text{Rh}^{3+}$. In most cases, the metals are accumulated in the roots, and where the metal was translocated to the tops, this was associated with toxic symptoms. Sequential extractions of tissue from plants treated with $\text{cis}[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ showed that in the leaves and floats almost half the platinum was insoluble and associated with alpha-cellulose and lignin, 16 % was removed by the enzyme pronase and can be considered to be associated with proteins or amino acids. In the roots, about a third of the Pt is insoluble and 9.5 % is removed by pronase. More Pt in the roots appeared in the fraction containing water soluble, low molecular weight materials (Farago and Parsons, 1994). Also the *Lumbriculus variegatus* was able to bio-concentrate Pt after exposure to H_2PtCl_6 (Veltz et al., 1994).

A number of studies report on the PGM concentration in human body fluids and tissue. Studies in the Australia have suggested that a major pathway of Pt into the human body is via the diet with an average dietary intake of 1.44 $\mu\text{g Pt}$ per day for adults (male: 1.73 $\mu\text{g day}^{-1}$; female: 1.15 $\mu\text{g day}^{-1}$). Platinum in material of plant and animal origin appears to be bioavailable (Vaughan and Florence, 1992). Toxic effects of metallic Pt, as emitted from by

automobile exhaust converters, are only expected if the Pt is bioavailable. The natural levels of Pt significantly fluctuate in human body fluids of various types. Values of 0.8-6.9 ng l⁻¹ and 0.56 µg l⁻¹ for blood, and 0.5-15 ng l⁻¹ and 0.18 µg l⁻¹ for urine have been reported (Vaughan and Florence, 1992).

In model experiments, a proper simulation substance was selected for substituting the particles, emitted by a three-way catalytic converter equipped engine (Artelt et al., 1998). The bioavailability of Pt from these particles and the form of Pt species in vivo were assessed. An in vitro solubility test showed that 10 % of Pt content from the model substance was soluble in physiological NaCl solutions. In some short-term animal tests, Pt was detectable in all the studied tissues (lungs, kidney, liver, spleen, stomach, adrenal glands) and body fluids. The contribution of the swallowed Pt (via oral application) to the Pt content of the matrices studied was very low; therefore, its contribution to the overall bioavailability is negligible. In another study (Artelt et al., 1999b), the model substance was applied to rats in tracheal instillation, inhalation, and by gavages. Pt was found in the blood, urine and faeces and all important part organs (liver, spleen, kidney, adrenals, stomach, femur). Based on the Pt content determination in the body fluids and all organs (except the lungs and faeces), it was calculated that up to 16 % of the Pt was retained in the lung 1 day after intratracheal instillation and up to 30 % of that the finely dispersed Pt deposited on average during 90 days inhalation in the lung was bioavailable. It was also reported that greater than 90 % of the bioavailable Pt was bound to high molecular weight compounds (80-800 kDa), most likely proteins. The authors suggested further investigations on the possible toxicity of the bioavailable Pt to humans.

Nygren et al. (1990) reported that the natural Pt levels in human blood range between 0.1 and 2.8 µg l⁻¹ (median: 0.6 µg l⁻¹). The median concentration of Pt determined in urine, scalp hair, sweat, saliva and fingernails were found to be 0.11, 3.02, 0.02, 0.07, and 19.0 µg l⁻¹, respectively. The informative values (0.49 and 1.80 µg l⁻¹ Pt) reported by Johnson et al. (1975) for composite urine samples from a population of California lies in this range. According to Schramel et al. (1995), the Pt concentration in urine samples of 10 different persons, collected during 24 hour periods, were between 1.2 to 35 ng l⁻¹ with a median value of 5.4 ng l⁻¹. These values are in the concentration interval accepted as “normal”, i.e. in the

range between 0.5 to 40 ng l⁻¹ (Schierl et al., 1994). Biomonitoring of traffic-exposed people showed no elevated daily urinary excretion (Schierl et al., 1994) compared to non-occupationally exposed people (Alt et al., 1993; Ensslin et al., 1994a). Schierl (2000) found a mean urinary Pt concentration of 6.5 ng per g of creatinine with a maximum value of 45 ng g⁻¹ after examining 178 individuals (non-exposed persons). Enhanced urinary Pt concentrations (above 20 ng g⁻¹) and long term excretions were observed for persons having dental gold alloys (Begerow et al., 1999; Begerow and Dunemann, 2000).

Begerow et al. (1997a) analysed the urine of 21 unexposed persons in Germany. The Pd levels ranged from 33 to 220 ng l⁻¹ (mean: 140 ng l⁻¹), while the Pt level was between 0.48 and 7.7 ng l⁻¹ (mean: 1.8 ng l⁻¹). On the other hand, Messerschmidt et al. (1992a) described the Pt concentration in urine of occupationally exposed persons in the range of 21 to 2900 ng l⁻¹. Nygren and Lundgren (1997) found increased Pt levels of blood in both graduate (2.2±1.7 µg l⁻¹) and staff nurses (3.8±4.0 µg l⁻¹), but low values in pharmacists (0.47±0.31 µg l⁻¹), in comparison with unexposed subjects (1.2±0.69 µg l⁻¹). The variation was, however, high for all groups. The mean Pt level in urine samples was 126±92 ng l⁻¹. On the contrary, in Germany an elevated level of urinary Pt was found in pharmacists (23 ng g⁻¹ creatinine) in comparison with a non-exposed control group (Ensslin et al., 1997). An average level of 0.6 ng l⁻¹ was found in the blood of citizens from Sydney (Vaughan and Florence, 1992). Caroli et al. (2001) evaluated the exposure of 310 school children to the PGMs in Rome, Italy. The mean concentration value of these metals in urine were found to be 7.5±5.4 for Pd, 0.9±1.1 for Pt, and 8.5±8.0 ng per g of creatinine for Rh. These values were found to be strongly associated with traffic density in the area of residence.

Freiesleben et al. (1993) investigated the solubility of Pd and Pt blacks (fine metal powders) in aqueous solutions containing biogenic substances. These finely dispersed materials mainly resemble the state of PGMs in catalytic converters. It was shown, for example, that the finely dispersed Pt significantly dissolved in the presence of adenosine triphosphate (ATP), the well-known bioactive compound of the living organisms, as well as human body.

Most analytical measurements have focused on the level of Pt in body fluids and tissues after administration of Pt-containing anticancer agents. The Pt concentrations in these samples are in order of 0.1-10 $\mu\text{g g}^{-1}$. On the contrary, the natural levels are two to three orders of magnitude lower. The analytical difficulties in measuring low concentrations of Pt in biological materials have led to a lack of data on baseline levels of the PGMs, which make health risk studies difficult on humans. The transformation mechanism of metallic Pt into bioavailable forms is still unknown and has to be investigated. The bioavailability of the particular essential, or toxic element depends on its chemical form (Cornelis et al., 1993) and investigations of Pt species in various matrices become a great challenge. The problem of environmental dispersion of PGMs should be carefully followed by decision-makers for its potential, and serious, large-scale consequences. Summarized data on the PGM concentrations in various biological matrices are listed in Table 13.

According to the above survey, plants can bioaccumulate anthropogenic PGMs to a diverse extent depending on the sort of the plant, the time interval of the contact with the emission source, the state, and dispersion of the PGM species (particularly the ability to complex formation), the local weather conditions. It was demonstrated that some animals and humans are also involved in the bioaccumulation process, which may cause a possible health risk.

Health effects of PGMs

Amongst PGMs, Pt provides an excellent example of the significance of speciation in metal toxicity. Platinum allergy is confined to a small group of charged compounds that contain reactive ligand systems, the most effective of which are chloride ligands (Cleare et al., 1976; WHO, 1991; Merget, 1999). Metallic Pt is considered to be biologically inert and non-allergenic, and since the emitted Pt is probably in metallic, or oxide form, the sensitising potential is probably very low. Platinum from the road dust, however, can be solubilized, and enters into waters, sediments, soils, and the food chain. Adverse occupational health effects in a photographic studio following exposure to complex Pt salts were first described in 1911 (Karasek and Karasek). In 1945, Hunter et al. conducted studies on precious metal workers in

four British Pt refineries, and reported 52 out of 91 persons having symptoms of sneezing, wheezing and shortness of breath.

The main hazard of the Pt can be seen in workers occupationally exposed to halogenated salts (Rosner and Merget, 1990), which includes in a high rate of occupational asthma and dermatitis in refinery workers (Dhara, 1984). It has been also reported that 50 % of the exposed workers are likely to developed immediate type respiratory hyper-sensitivity reaction following exposure to platinum salt such as ammonium tetrachloroplatinite(II), or ammonium hexachloroplatinate(IV), used in the production of industrial catalysis (Hughes, 1980; Roberts, 1951). Latency from first contact with Pt to the development of symptoms varied from a few months to 6 years. It has also been shown that sensitised workers removed immediately from further contact with Pt salts showed no evidence of long-term effects. The Health and Safety Executive (1990) lists watering of eyes, sneezing, tightness of chest, wheezing, breathlessness, cough, eczematous and urticarial skin lesions, sign of mucus membrane inflammation, as a typical of Pt salt sensitisation. In addition, some Pt complexes can bind to N and S in proteins producing a possible reduction in enzymatic activity (Helmers et al., 1994).

Platinum compounds, especially the soluble salts, are toxic, and chronic industrial exposure to these compounds is responsible for the development of a syndrome known as *Platinosis*, which is characterized by respiratory and cutaneous hypersensitivity (Brubaker et al., 1975). Employees exposed during the production and recycling of Pt based catalytic converters revealed Pt levels in urine and blood up to 100 times higher compared to non-exposed control individuals (Zereini and Alt, 1999). In addition, some Pt coordination complexes that are used as tumour treatment agents, are mutagenic, and are suspected human carcinogens (Leopold et al., 1979). Application of cis-dichlorodiamine Pt as an anticancer agent has been associated with the development of systematic anaphylactic and cutaneous immediate hypersensitivity reactions in some patients (von Hoff et al., 1976; Kahn et al., 1975). On the contrary, Pt is non-toxic and non-allergenic in its metallic state.

Complex salts of Pt, especially chloroplatinates, are potential sensitizing agents (Hughes, 1980; Roberts, 1951). Chloroplatinates irritate the skin and mucous membranes. They can cause allergic reaction in high rates of occupational asthma and dermatitis (Schulze-

Werninghaus et al., 1985). The allergic response of Pt increase with increasing number of chlorine atoms, the most potent compounds being hexachloroplatinic(IV) acid and its ammonium and K salts, and the K and Na tetrachloroplatinite(II). There is epidemiological evidence that the sensitizing potential of Pt compounds is restricted to halogenated compounds (Linnet and Hughes, 1999). Contact hypersensitivity was also observed on mice by the administration of hexachloroplatinate (Schuppe et al., 1997).

Non-halogenated complexes and neutral complexes, including in the anti-cancer drug, cisplatin $[(\text{NH}_3)_2\text{Pt}(\text{Cl}_2)_2]$, are not allergenic, perhaps because they do not act as haptens (i.e. chemical compounds, which can bind to a biological macromolecule, e.g. a protein). Pharmacodynamic, as well as toxic properties of cisplatin are due to its specific planar structure (intra-strand DNA cross-linking activity), which is exceptional compared to other Pt compounds. This is particularly true for nephro-, myclo-, and ototoxic side effects observed on patients treated with therapeutic doses, and additionally, mutagenic and carcinogenic effects observed in experimental animal studies (WHO, 1991). Further occupational exposure in sensitized subjects leads to persistence, and sometimes to progressive deterioration of asthma, irrespective of the reduction of exposure to the specific sensitizer.

The administration of Pt drugs often accompanied by undesirable side-effects including in nausea (See-Lasley and Ignoffo, 1981), hearing loss (Evans et al., 1982; Loehrer and Einhorn, 1984) and nephrotoxicity (Safirstein et al., 1986). There is also concern about the mutagenicity and the potential carcinogenicity of these drugs especially in relation to occupational exposure (IARC, 1981; Vaughn and Christensen, 1985). Tumoral cells are more prone to attack by the Pt containing substances than normal cells as a consequence of higher permeability of the former *in vivo*, as well as to the high dose, short-term conditions of administration (short of acute exposure), which leave the healthy cells practically unaffected. This situation may dramatically change as the permanent presence of much lower concentration of Pt in the environment completely switches the scenario to that of chronic exposure, the impact of which on healthy cells of living organism is partly unknown and partly worrisome (Ensslin et al., 1994a, 1994b).

Nursing staffs are evidently concerned about the risk of hazardous exposure of Pt due to the increasing use and contact with anti-neoplastic drugs. Many studies have indicated that

increased urine mutagenicity, chromosome aberrations and sister chromatid exchange as well as increased hairloss, increased spontaneous abortions, and malformed offspring among nursing staff handling cytotoxic drugs (Waksvik et al., 1981; Kolmodin-Hedman et al., 1983; Nikula et al., 1984; Bingham, 1985; Hemminki et al., 1985; Selevan et al., 1985; Vaughn and Christensen, 1985; Stücker et al., 1986). One drawback of the general methods used in examining such problems, however, is that they lack in specificity. The search for a biological parameter reflecting the possible damage induced by these drugs is ongoing. Several studies have focused on different cytogenetic effects, leading to contradictory results. However, only limited data combine exact information on the degree of drug exposure, incorporation and potential cytogenetic damage.

Halogenated Pt compounds have been reported as potent respiratory allergens leading to rhinitis, conjunctivitis, asthma and urticaria (Rosner and Merget, 1990). Sensitization level of $0.1 \mu\text{g m}^{-3}$ in air for soluble platinum compounds was reported (Rosner and Merget, 2000). Certain Pt compounds are also known to be cytotoxic and have mutagenic and carcinogenic effects and have some effects on microorganisms at very low concentration (WHO, 1991, Bünger et al., 1996; Gebel et al., 1997; Lantzsch and Gebel, 1997). The first inhalation study on Pt and its compounds using radioactive labeled materials, was reported by Moore et al. (1975a). Platinum and its compounds were mainly retained in the respiratory tract (lungs, *Trachea*); moreover, significant concentrations were also determined in the kidneys and femur. The whole body retention after 24 hours depended on the applied Pt species, and decreased according to the queue ($\text{PtCl}_4 > \text{Pt}(\text{SO}_4)_2 > \text{PtO}_2 > \text{Pt}$) (Moore et al., 1975b; see also Artelt et al., 1999b).

Micro-toxicity tests have shown that the EC_{50} of platinum chloride for photo bacterium phosphoreum is $25 \mu\text{g l}^{-1}$, which is much lower than that of Cu ($200 \mu\text{g l}^{-1}$) (Wei and Morrison, 1994a). The diagnosis of platinum-related occupational disease can be confirmed by skinprick tests using minute doses (10^{-2} to $10^{-8} \text{ mol l}^{-1}$) of Pt salts, although such tests can be hazardous. An immunological study reported on the allergenic effects of particulate exhaust on workers already sensitive to Pt salts. Skin prick tests, in a preliminary study, only on three subjects, were negative up to a concentration of $5 \mu\text{g ml}^{-1}$, which would normally be sufficient to elicit a response (Cleare, 1977). Metallic Pt is considered to be non-

allergenic, since the emitted Pt from catalysts is probably in the metallic, or oxide form, and, thus, its sensitizing potential is probably very low.

Topical exposure of mice to respiratory sensitizing Pt salts elicited a similar quality of immune response to that induced by epicutaneous application of organic allergens, such as toluene diisocyanate, trimellitic anhydride, or cyanuric chloride (Dearman et al., 1998). Despite an association, in some cases, between respiratory symptoms and the production of specific IgE antibody and elevated total serum IgE (Baker et al., 1990; Cromwell et al., 1979; Murdoch et al., 1986), non-specific effects have been reported (Merget, 1999; Merget et al., 1999), even after the allergen avoidance (Merget et al., 1994). Hexa- and tetra-chloroplatinum salts have been shown to act synergistically with classical adjuvants to enhance IgE production and specific IgE response to unrelated proteins in rats (Murdoch and Pepys, 1984). It has been demonstrated, however, that these Pt salts and cis-dichlorodiammine platinum(II) are potent immunogens in mice, involving in vigorous proliferation, when administered subcutaneously in the popliteal lymph node assay (Schuppe et al., 1992).

Increased Pt concentrations, compared to natural levels, were reported not only in human body fluids (blood, urine, etc.) and tissue of occupationally exposed persons (Rosner and Merget, 1990), but also in body fluids of non-occupationally exposed persons (Vaughan and Florence, 1992; Begerow and Dunemann, 1996; Begerow et al., 1997a, 1997b, 1997c). Unfortunately, the toxicity of bioavailable, anthropogenic Pt is not very clear (Pallas and Jones, 1978; Rosner et al., 1991; Ballach and Wittig, 1996; Nachtigall et al., 1996). On the other hand, certain Pt species are known to exhibit an allergenic potential (Summer, 1990; Schulze-Werninghaus et al., 1990), which raises questions for the health effect from the long-term exposure of low-level Pt compounds.

With regards to the other Pt group metals, Rh occurs in a lower amount in catalyst than Pt. On the other hand, palladium gains an increasing application in catalytic converters, and Ir was just recently introduced in Japan, as the so-called “DeNO_x” catalysator, with the aim to drastically reduce the nitrogen oxide emission in the exhaust of lean burning engines.

For halogenated Pd and Rh salts (PdCl₂ and RhCl₃), increased tumor incidences were observed in a lifetime drinking-water carcinogenicity study on mice (Schroeder and Mitchener, 1971). However, due to major methodological deficiencies (e.g. only one dose

applied; higher longevity in treated as compared to control group; number of the tumors pooled despite the sex-specific differences), the validity of this study was questioned (Merget and Rosner, 2001).

As regards the sensitizing potential of the other PGMs, there is no evidence for a higher potency than Pt salts. On the other hand, there is a striking difference between metallic Pt and Pd, since metallic Pd causes contact dermatitis. However, this effect can not be projected to the respiratory sensitizing potential of Pd and its compounds. Immediate type reactions to Pd have been reported only on refinery workers sensitized to Pt, and limited cross-reactivity between both metals (Murdoch and Pepys, 1987). The latter study showed a low prevalence of sensitization to PGMs other than Pt. Bergman et al (1995) reported one case of an occupational Ir salt immediate-type allergy without Pt salt allergy.

Studies over more than ten years have shown that the allergenic potential of Pd has been underestimated. Allergic reaction was first reported in connection with the use of dental alloys rich in Pd (Van Ketel and Niebber, 1981; Castelain and Castelain, 1987). Similar observations were made in skin test with Pd chloride, which also revealed a distinct cross sensitivity to nickel. About 90 % of those tested, reacting against Ni also demonstrated sensitivity towards Pd (Olivarius and Menné, 1992). Occupational asthma caused by Pd metal reported only in one case (Daenen et al., 1999).

Conclusion

Platinum group elements, mainly released by automotive catalytic converters, are continuously increasing in environmental matrices over the time. It is still under discussion, whether the emitted PGMs are toxic for living organisms, and human beings. It is known that the metallic form of these elements is inert as far as biological reactions are concerned, but that, in contrast, some of their compounds, such as hexachloroplatinate, and tetrachloroplatinite complexes, etc., are among the most potent allergens and sensitizers. Hence, the potential health risk from these elements would have to be taken in consideration, which further raise questions for the possible risk of exposure for those living in urban environments, or along major highways. In this context, the transportation, transformation, and bioavailability of PGMs play a key role, especially, in the view of some contradictory

results of the relevant literature (eg. estimates on the soluble PGM portion of the evolved exhaust, and interpretation on the PGM uptake by plants). All the above topics need further investigation (both experimental and model), partly on the base of health studies of PGM salts, to reach a better understanding of the behaviour of PGMs in the environment.

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Figure 1 Catalytic converter



Table 1 Platinum group metal demand by application (worldwide)

Application	1999 (kg)	2000 (kg)
PLATINUM		
Autocatalysts: gross	45600	51000
Autocatalysts: recovery	-12000	-13000
Jewellery	79400	83300
Industrial	38400	41400
Investment	5100	-1420
Total Demand (Pt)	159000	146000
PALLADIUM		
Autocatalysts: gross	166700	146000
Autocatalysts: recovery	-5530	-6520
Dental	31500	24700
Electronics	56100	58600
Other	16600	15000
Total Demand (Pd)	265000	238000
RHODIUM		
Autocatalysts: gross	14400	16000
Autocatalysts: recovery	-1870	-2240
Chemical	964	992
Electronics	170	170
Glass	851	1050
Other	312	312
Total Demand (Rh)	14900	16200
RUTHENIUM		
Chemical	2440	1930
Electrochemical	2040	2270
Electronics	5560	6580
Other	1160	1360
Total Demand (Ru)	11200	12100
IRIDIUM		
Automotive	964	397
Chemical	198	170
Electrochemical	794	680
Other	936	1450
Total Demand (Ir)	2890	2690

Table 2 Platinum demand by application in Europe (kg)

Platinum demand	1992 (kg)	1994 (kg)	1996 (kg)	1998 (kg)	2000 (kg)
Autocatalyst: gross	16300	17200	14600	15500	17900
Autocatalyst: recovery	-142	-284	-567	-851	-1130
Chemical	1420	1420	1700	1700	2410
Electrical	851	709	709	1280	2270
Glass	425	851	1130	709	709
Investment:small	992	1276	142	142	0
Jewellery	2410	2840	3540	4540	5670
Petroleum	567	709	425	425	284
Other	1560	1840	2130	2410	2840
Totals (Pt)	24400	26500	23800	25800	30900

Table 3 Palladium demand by application in Europe (kg)

Palladium demand	1992 (kg)	1994 (kg)	1996 (kg)	1998 (kg)	2000 (kg)
Autocatalyst: gross	1130	7370	24400	38800	51600
Autocatalyst:recovery	0	0	142	-142	-425
Chemical	2100	1700	1840	1840	2690
Dental	8500	7230	7230	5950	3120
Electronics	5950	7230	8500	7660	7370
Jewellery	992	851	851	1420	1280
Other	425	709	567	709	567
Totals (Pd)	19100	25100	43200	56300	66200

Table 4. Direct determination of PGMs from car exhaust fumes

Catalyst	Operation condition	PGMs emission	Reference
Pellet-type	48 km h ⁻¹ 96 km h ⁻¹	Pt: 1.2 µg km ⁻¹ Pt: 1.9 µg km ⁻¹	Hill and Mayer, 1977
Three-way	Idle	Pt: 67 ng m ⁻³	Rosner and Hertel, 1986
Three-way	60 km h ⁻¹ 100 km h ⁻¹ 140 km h ⁻¹ US-Cycle 75	Pt: 3.3±1.6 ng m ⁻³ Pt: 11.9±5.8 ng m ⁻³ Pt: 39.0±16.6 ng m ⁻³ Pt: 6.4±6.3 ng m ⁻³	König et al., 1992
Three-way (Pt-Rh)	140 km h ⁻¹	Pt: 120 ng m ⁻³ Rh: 20 ng m ⁻³ Pd: 0.3 ng m ⁻³ Ir: 0.02 ng m ⁻³	Lüdke et al., 1996
Three-way	Engine: 1.8 l, 66kW New converter: at 80 km h ⁻¹ at 130 km h ⁻¹ Old converter: at 80 km h ⁻¹ at 130 km h ⁻¹	Pt: 7-124 ng km ⁻¹ (mean) Pt: 12 ng km ⁻¹ Pt: 90 ng km ⁻¹ Pt: 9 ng km ⁻¹ Pt: 18 ng km ⁻¹	Artelt et al., 1999a
Three-way (fresh)			Palacios et al., 2000b
a) Petrol		Pt: 100 ng km ⁻¹ Pd: 250 ng km ⁻¹ Rh: 050 ng km ⁻¹	
b) Diesel		Pt: 400-800 ng km ⁻¹	

Three-way (aged:
30 000 km)

a) Petrol

Pt: 6-8 ng km⁻¹

Pd: 12-16 ng km⁻¹

Rh: 3-12 ng km⁻¹

b) Diesel

80 km h⁻¹ constant
speed

Pt: 6.3-7.5 ng km⁻¹

Pd: 1.2-1.9 ng km⁻¹

Rh: 0.6-1.2 ng km⁻¹

Pt: 11-58 ng km⁻¹

Pd: 2-24 ng km⁻¹

Rh: 1.5-7 ng km⁻¹

Fresh gasoline
catalyst
Pt/Pd/Rh
Pd/Rh

Pt: 27-313 ng km⁻¹

Pd: 6-108 ng km⁻¹

Rh: 8-60 ng km⁻¹

Moldovan et al.,
1999

Diesel Pt

Pt: 47-170 ng km⁻¹

Three-way Pd-Rh
gasoline

Pd: 2.59-9.38 µg l⁻¹

García et al.,
2001

Diesel Pt

Pd: 11.25 µg l⁻¹

Three-way
Gasoline

Pt: 10.2 ng km⁻¹

Pd: 14.2 ng km⁻¹

Rh: 2.6 ng km⁻¹

Rauch et al.,
2002

Diesel

Pt: 223 ng km⁻¹

Pd: 75.8 ng km⁻¹

Rh: 33.7 ng km⁻¹

Table 5 Particulate (p), soluble (s) and total (t) PGMs (ng km^{-1}) in exhaust fumes from different automotive catalytic converters as a function of the engine ages (driven kms)

		Type of catalytic converter			
		Pt-Pd-Rh	Pd-Rh	Pt (c1)	Pt (c2)
0 km					
Pt	p	99.8±82	99.7±119	809±1441	402±785
	s	1.6±2.2	2.6±1.7	3.1±2.6	1.4±2.1
	t	101±85	102±119	812±1443	404±785
Pd	p	256±380	243±378	213.9±344.9	25.9±49
	s	8.7±3.9	2.8±2.3	2.7±2.9	1.2±0.9
	t	264±378	246±378	217±345	27.1±49
Rh	p	63.3±88	36.6±50	181±286	79.9±145
	s	2.6±1.7	1.4±1.4	3.2±1.8	1.6±1.6
	t	65.9±89	38±52	184±288	81.5±145.2
30000 km					
Pt	p	5.6±2.2	5.6±1.7	150±60	108±105
	s	0.7±0.6	2.6±7.4	2.4±1.6	1.9±1.4

	t	6.3±2.5	8.2±8.0	152±60	110±106
Pd	p	5.3±3.5	7.4±2.6	39.5±19	73.5±71
	s	6.7±6.4	8.5±7.5	6.4±5.5	8.0±9.7
	t	12±5.7	15.9±5.1	45.9±23	81.5±75
Rh	p	1.7±0.8	2.5±0.8	23.3±11	36.4±44
	s	2.0±2.1	9.7±17	2.5±1.6	2.5±3
	t	3.7±2.1	12.2±15	25.8±11	38.9±44

c1 catalyst (Pt):

c2 catalyst (Pt):

(Palacios et al., 2000a, 2000b)

Table 6 Platinum emission by cars

	D 1994	D 1996	A 1996	NL 1996
Pt emission by cars				
Number of cars	32 000 000	32 000 000	3 593 600	5 740 500
With VEC	12 800 000	19 200 000	1 607 700	3 307 300
% with VEC	40.0	60.0	44.7	57.6
Kilometers/car	15 000	15 000	14 400	13 540
Total kms (VEC only)	1.92x10 ¹¹	2.88x10 ¹¹	2.31x10 ¹⁰	4.49x10 ¹⁰
Emission ($\mu\text{g km}^{-1}$)	0.65	0.65	0.5	0.5
Total emission by cars (kg)	124.8	187.2	11.6	22.5

Abbreviations: D – Germany, A – Austria, NL – The Netherlands, VEC – vehicle exhaust catalyst.

Table 7 Emission of platinum by hospitals

	D 1994	D1996	A 1996	NL 1996
Total hospital beds (approx.)	645 000	645 000	77 500	60 000
Maximum medical performance				
	45 000	45 000	6 500	N/A
Pt per bed and year (mg)				
- maximum medical service	154.0	130.4	58.7	22.3
- medium medical service	14.0	14.0	N/A	N/A
Pt emissions by hospitals (kg yr ⁻¹)				
- maximum medical service	6.9	5.8	0.38	1.3
- medium medical service	8.4	8.4	N/A	N/A
Total emissions by hospitals (kg yr ⁻¹)	15.3	14.2	N/A	N/A
All hospitals as maximum medical service	99.3	84.1	4.6	1.3

Abbreviations: D – Germany, A – Austria, NL – The Netherlands, N/A – no data available.

Table 8 PGM content in airborne samples

City/Country	Other specification	PGM concentration (pg m^{-3} , if not indicated, otherwise)	Reference
California, USA	-	Pt: <0.05	Johnson et al., 1975
California	-	Pd: <0.06	Johnson et al., 1976
Belgium, Italy	-	Pd: <0.7	Schutysen et al., 1977
Tsukuba, Japan	-	Pt: 0.014-0.184 $\mu\text{g g}^{-1}$	Mukai et al., 1990
Dortmund, Germany	urban environment	Pt: 0.02-5.1	Alt et al., 1993
California	PM ₁₀	Pd: 1	Lu et al., 1994
Caesarea, Israel	PM _{2.5} (1993)	Pd: 3.3	Gertler, 1994
Bruck/Mur, Austria	Tanzenberg tunnel dust	Pt: 13.0±3.8	Wegscheider and Zischka, 1993
Munich, Germany	bus, tramway (1993-94)	Pt: 0-43.1 (mean: 7.3)	Schierl and Fruhmann, 1996
Graz, Austria	tunnel dust	Pt: 11.0±3.8	
Chicago, USA	(1990)	Pd: 12 700 (mean)	Scheff et al., 1997
Chernivtsi, Ukraine	(1990)	Pd: 56 600 (mean)	
Stuttgart, Germany	urban area (1997)	Pt: 68 ng g ⁻¹	Helmers and Mergel, 1998
Stuttgart	urban area (1997)	Rh: 8 ng g ⁻¹	
Czech Republic	various observation sites	Pt: 9-62 Pd: 30-280	Vlašánková et al., 1999

Italy		Pt: 6.4-38.8	Caroli et al., 2000
Germany	background level	Pt: <2	Rosner and Merget, 2000
Germany	-	Pd: 9-106	
Munich, Germany	-	Pt: 4.42-42.4 (mean: 13.6)	Dietl et al., 2000
Berlin	urban environment (1997)	Pd: 0.2-14.6	Tilch et al., 2000
Munich	bus, tramway (1993-94)	Pt: 7.3 (mean)	Schierl, 2000
Munich	bus, tramway (1995-96)	Pt: 21.5 (mean)	
Rome	urban sites (heavy traffic)	Pd: 21.2-85.7	Petrucci et al., 2000
		Pt: 7.8-38.8	
		Rh: 2.2-5.8	
Copenhagen, Denmark	heavy traffic (1993)	Pt: 13	Probst et al., 2001
Copenhagen	heavy traffic (1995-1997)	Pt: 250-2740	
Madrid, Spain		Pt: <0.1-57.1 (mean: 12.8)	Gómez et al., 2001
Madrid		Rh: <0.2-12.2 (mean: 3.3)	
Germany	1988	Pt: 91.5	Zereini et al., 2001a
	1998	Pt: 464	
	1988	Rh: 7.5	
	1998	Rh: 31.5	

Table 9 Comparative results of Pt and Pd in garden soil (0-5 cm) and road dust in Nottingham (Hutchinson et al., 2000)

Year	Sample	n	Pt (ng g ⁻¹)		Pd (ng g ⁻¹)	
			range	mean	range	mean
1982	soil	42	0.27-1.37	0.61	0.64-0.99	0.05
1996	soil	42	0.19-1.33	0.80	0.21-1.11	0.18
1982	road dust	10	0.46-1.58	0.90	0.69-4.92	1.24
1996	road dust	8	0.82-6.59	2.29	0.19-1.43	0.75
1998	road dust	20	7.3-298	69.55	5.6-556	92.95

n – number of parallel determinations

Table 10 PGM concentrations in soil and road dust

Samples	Location	Other conditions	Concentration (ng g ⁻¹ , if not indicated, otherwise)	References
Roadside dust	San Diego	heavy traffic (1985) (freeways) light traffic (residential streets)	Pd: 38-280 Pt: 100-680 Pd: 15-24 Pt: 300	Hodge and Stallard, 1986
Filter dust	Hannover		Pt: 0.19	Hoppstock et al., 1989
Dust	Dortmund		Pt: 12	Beinrohr et al., 1993
Street dust	Graz, Austria		Pt: 14.5	Wildhagen and Krivan, 1993
Roadside soil	Germany	motorway	Pt: 27	Zereini et al., 1993
Roadside dust	Germany		Pt: ≤100	Zereini et al., 1994
Roaddust	Germany	from roadside grass	Pt: 5-8	Helmers et al., 1994
Sewage sludge ash	Germany	from incinerator	Pt: 605	
Road dust	Göteborg	car park (1991) kerbside	Pt: 26 ng m ⁻² Pt: 1.28 µg m ⁻²	Wei and Morrison, 1994a
Tunnel dust	Austria	tunnel ceiling	Pt: 68.2	Schramel et al., 1995
Continental crust			Pt, Pd: 0.4 Rh: 0.06	Wedepohl, 1995
Roadside dust	Germany	highway	Pd: 1-146	Schäfer et al., 1996
Road dust	SE Germany	16000 car/day	Pt: 14 ng m ⁻² daily	Laschka et al., 1996

Soil	Richmond (1996)	minor/intermediate roads	Pt: 0.3-8	Farago et al., 1996
Dust	Richmond (1996)	major road intersection (A3)	Pt: 0.42-29.8	
Soil	Kent, UK (1996)	botanic garden	Pt: 0.8-1.6	
Roadside dust	Belgium		Pt: 12.04	Parent et al., 1996
Soil			Pt: 79.4	
Roadside dust	Frankfurt	(1995)	Pt: 170	Zereini et al., 1997a
Roadside dust	Frankfurt	(1994)	Pd: 6-117	Zereini et al., 1997b
			Rh: 1-26	
Cultivated soil	Germany	garden, agriculture, mould	Pt: 0.15-3.9 (mean:1.1)	Alt et al., 1997
Uncultivated soil	Germany	mountain, forest, coast	Pt: 0.03-0.26 (mean:0.14)	
Roadside soil	Germany	motorway	Pt: 15.6-31.7 (mean: 20.9)	
Soil	Germany	-	Pt: 25.3-253	Cubelic et al., 1997
			Pd: 1.2-12.5	
			Rh: 4.8-39.7	
Dust		highway	Pt: 7-198	
			Rh: 8-31	
Dust	Germany	tunnel (1997)	Pt: <730	Helmerts and Mergel, 1998
			Rh: <60	
Tunnel dust	Japan	(1987)	Pd: 297	Helmerts et al., 1998
Tunnel dust			Pt: 170	
			Pd: 20	

Roadside soil	Stuttgart, Heidelberg	highway (background)	Pt: 10 (max) Rh: 35 (max)	Schäfer and Puchelt, 1998
Roadside soil	Hanau, Germany	near motorway (1995)	Pt: 23-112	Zereini et al., 1998
Soil	Germany	highway (southeast)	Pt: 0.9-200	Schäfer and Puchelt, 1998
Roadside dust			Pt: 23 ng m ⁻²	Schäfer et al., 1999
Road sediment			Pt: 30-180 Pd: nd-28 Rh: 5-45	
Road dust	Karlsruhe, Germany	(1997)	Pt: 112-169	Schäfer et al., 1999
Road dust		motorway	Pt: 340	Beyer et al., 1999
Road dust	Sweden	-	Pt: 213 ng g ⁻¹ Pd: 56 ng g ⁻¹ Rh: 74 ng g ⁻¹	Rauch et al., 1999
Road dust	Italy		Pt: 1.9-62.2 ng g ⁻¹	Caroli et al., 2000
Road dust	Nottingham	(1998) n=20	Pt: 96.8	Hutchinson et al., 2000
Road dust	Birmingham	(1997) n=14	Pt: 6.48	
Road dust	Nottingham	(1998) n=20	Pd: 92.9	
Soil along motorways	Frankfurt	n=69	Pt: 72 Pd: 6 Rh: 18	Zereini et al., 2000

Soil in city area	Frankfurt	n=10	Pt: 46 Pd: 4 Rh: 9	Zereini et al., 2000
Road tunnel dust	Theatre (Frankfurt)	1994 summer	Pd: 40.3±12.0	Boch et al., 2002
	Harbor (Frankfurt)	1994 summer	Pd: 113.7±35.4	
Road tunnel dust	Candid (Munich)	(August 1994)	Pd: 13.5±3.7	Boch et al., 2002
	Trappentreu	110 000 car/day (1994)	Pd: 17.7±4.1	
	Landshuter Allee	100 000 car/day (1994)	Pd: 21.8±3.5	
Road tunnel dust	Candid (Munich)	94 000 car/day (Aug 1997)	Pd: 41.6±12.2	Schuster et al., 2000
	Trappentreu	126 000 car/day (1998)	Pd: 32.9±10.1	
	Landshuter Allee	118 000 car/day (1998)	Pd: 100.5±15.1	
Road tunnel dust	Candid (Munich)	(February 2001)	Pd: 138.2±13	Boch et al., 2002
	Trappentreu	(2001)	Pd: 281.6±28.8	
	Landshuter Allee	(2001)	Pd: 265.4±9.9	
Tunnel dust	Styria, (Tanzenberg tunnel) (Austria)	Ventilation shaft, 1994	Pt: 55 Rh: 10.3 Pd: 4.0	Schramel et al., 2000
Tunnel dust	Styria (Tanzenberg tunnel) (Austria)	Ventilation shaft, 1998	Pt: 81 Rh: 12.8 Pd: 5.5	Schramel et al., 2000
Soil	Frankfurt	(1996) Highway A66, A67	Pt: 45	Schramel et al., 2000

Road dust	Austria	highway tunnel	Rh: 7 Pt: 47±3.1 Pd: 3.2±0.4 Ru: 2.0±0.2 Ir: 0.16±0.06	Müller and Heumann, 2000
Soil	Mainz, Germany	0.6 m from highway(BAB66)	Pt: 87±17	Müller and Heumann, 2000
		1.8 m	Pt: 8.7±1.5	
		3.0 m	Pt: 2.5±1.4	
Soil	Mainz, Germany	0.6 m from the highway	Pd: 7.2±1.5	Müller and Heumann, 2000
		1.8 m	Pd: 1.2±0.3	
		3.0 m	Pd: 1.1±0.5	
Soil	Mainz, Germany	0.6 m from the highway	Ru: 3.6±0.5	Müller and Heumann, 2000
		1.8 m	Ru: 2.3±1.0	
		3.0 m	Ru: 1.6±1.0	
Soil	Mainz, Germany	0.6 m from the highway	Ir: 0.37±0.09	Müller and Heumann, 2000
		1.8 m	Ir: 0.16±0.07	
		3.0 m	Ir: 0.13±0.07	
Road sediment	Darmstadt, Germany	near roads, highways	Pd: 7.2-58.6	Patel et al., 2000
Road sediment	Göteborg	1998	Pt: 157 (171)	Rauch et al., 2000a
		<63µm particle fraction,	Pd: 472 (395)	
		(63-250 µm particle fraction)	Rh: 60.4 (46)	

Road sediment	Göteborg	1984 <63 μm particle fraction/ (63-125 μm particle fraction)	Pt: nd (nd) Pd: 43.3 (54.1) Rh: 2.82 (1.65)	Rauch et al., 2000a
Road dust	Rome	urban sites (heavy traffic)	Pd: 102-504 Pt: 14.4-62.2 Rh: 1.9-11.1	Petrucci et al., 2000
Soil	Nottingham	highway (1982) (1996)	Pt: 0.05-1.37 Pt: 0.19-1.33	Farago et al., 2000
Soil	Birmingham	highway (1982) (1996)	Pt: 0.09-4.13 Pt: 0.05-4.45	Farago et al., 1996
Urban dust			Pt: 525	Zereini et al., 2001a
Parking place dust		Indoor	Pt: 232 Pd: 108	Zereini et al., 2001a
Tunnel dust			Pt: 141 Pd: 48	Zereini et al., 2001a
Road dust	Göteborg, Sweden	1998, heavy traffic road (<63 μm particle fraction)	Pt: 196 \pm 22 Rh: 93 \pm 15 Pd: 80 \pm 13	Motelica-Heino et al., 2001
Soil	Mexico City (Insurgentes/ Periférico)	high traffic (stop and go) (200 cars min^{-1} at rush hours)	Pt: 307.5-332.7 Pd: 53.2-74 Rh: 26-39.1	Morton et al., 2001

	(Insurgentes/ Sta. Teresa)	low density (stop and go) (60 cars min ⁻¹ at rush hours)	Pt: 2.2-8.5 Pd: 12.2-32.4 Rh: 0.7-2.7	Morton et al., 2001
	(Periférico)	high traffic (constant speed) (110 cars min ⁻¹ at rush hours)	Pt: 91.2-172.4 Pd: 15.2-82.7 Rh: 4.7-18.4	
	(Periférico/ Viaducto)	high traffic (constant speed) (180 cars min ⁻¹ at rush hours)	Pt: 161.7-207.7 Pd: 62.5-101.2 Rh: 18.2-22.7	
Road dust	Madrid	six sampling locations	Pt: 31-2252 (mean: 317) Rh: 11-182 (mean: 74)	Gómez et al., 2001
Road dust	Madrid	ring road, city centre (<65 µm)	Pd: 39-191 ng g ⁻¹	García et al., 2001
Roadside dust	Scotland	dual carriageway/motorway	Pt: 13-335	Higney et al., 2002
Surface soil		far of roads	Pt: <1.0	
Dust	East Kilbride town	residential area	Pt: 1.8-11.8	
Urban soil			Pt: 3.1 Pd: 1.66	Dongarrá et al., 2002
Soil	Rome	1992 2001	Pt: 0.8-6.3 Pt: 7.0-23.7	Cinti et al., 2002
Street dust	Germany	Saarbrücken	Pt: 178±20 Pd: 107±7	Kovacheva and Djingova, 2002

Road dust	Germany	Motorway (A-1)	Pt: 283±40 Pd: 59±2	Kovacheva and Djingova, 2002
		Motorway (A-61)	Pt: 307±60 Pd: 95±8	
		Highway (B-262)	Pt: 252±40 Pd: 68±3	
Tunnel dust	Austria (Styria)	Sampling from the ceiling	Pt: 62.5±3.8 Pd: 17.4±2.3 Rh: 9.4±0.8	Köllensperger et al., 2000
Road dust	Poland (Białystok)	Main crossroad (town)	Pd: 36.6	Godlewska and Zaleska, 2002
Road dust	Hungary (Budapest)	streets with heavy traffic	Pt: 0.076-0.667 ng/m ² /day	Dani et al., 2001
Road soil (surface)	Hungary (Budapest)		Pt: 4.09-89.7	
Road soil (5cm depth)	Hungary (Budapest)		Pt: 1.51-78.2	
Road dust	Germany, Karlsruhe	road B10 (heavy traffic)	Pt: 101.3 Rh: 18.7 Pd: 21.3	Sures et al., 2001

Table 11 PGM concentrations in vegetation

Samples	Location	Other parameters	Concentration (ng g ⁻¹)	References
Radish, barley, tobacco	Stuttgart	entire plant (unpolluted)	Pt: ≤40	Alt et al., 1988
Radish	Stuttgart	entire plant (polluted)	Pt: 1450-2070000	
		root	Pt: 530	
		leaves	Pt: 180	
Barley	Stuttgart	root (polluted)	Pt: 5670000	
		ear	Pt: 4380	
		leaves	Pt: 29800	
Tobacco	Stuttgart	entire plant (polluted)	Pt: 1050000	
		root	Pt: 110000	
		leaves	Pt: 23300	
Clover			Pt: 2.26	
Rye grass			Pt: 26.7	
Bean	Belgium	stalk	Pt: 11.05	Parent et al., 1996
		leaves	Pt: 3.76	
Plants		ultrabasic soil	Pt: 100-830	Valente et al., 1982

Corn	Germany	Stuttgart	Pt: 80	Hoppstock et al., 1989
Rye grass	Hannover	control	Pt: 0.32	
Rye grass	Hannover	treated with car exhaust	Pt: 1.5	
Beans	Dortmund		Pt: 550	Beinrohr et al., 1993
Beans	Dortmund		Pt: 130	Lee et al., 1993
Corn	Graz, Austria		Pt: 642	Wildhagen and Krivan, 1993
Roadside grass	Stuttgart	60 000 car day ⁻¹	Pt: 2.9	Helmers et al., 1994
	Stuttgart	0.2 m road distance	Pt: 4.6	
Pine, birch, grass	Germany	80-120 000 car day ⁻¹ (1995/96)	Pt: 12 Pd: 2 Rh: 2	Helmers, 1997
Salad, spinach, green kale	-	-	Rh: 0.2-0.9	Alt et al., unpublished results
Roadside grass	Stuttgart	60 000 car day ⁻¹ (1993)	Pt: 2.9	Helmers et al., 1994
		0.2 m off the road (1994)	Pt: 4.6	
Roadside grass	Ghent, Belgium	near the motorway (1995)	Pt: 1.4-1.7	Hees et al., 1998
	Siegen, Germany	near the motorway (1996)	Pt: 17.0-95.6	
Grass	Germany	road side (1994)	Pt: 3.61	Helmers and Mergel, 1998

		(~96 000 car day ⁻¹)	Rh: 0.65	
		road side (1997)	Pt: 10.6	
			Rh: 1.54	
		unpolluted areas (1997)	Pt: <0.03	
			Rh: <0.03	
Grass		rural site	Pt: 0.1-0.3	Angerer and Schaller, 1994
Roadside grass	Munich	0.2 m from motorway	Pd: 1.31	Schuster et al., 2000
		0.5 m from motorway	Pd: 0.70	
		1.0 m from motorway	Pd: <0.3	
Tree bark	Sheffield, London	rural, industrial areas, cities	Pt: 0.07-5.4	Becker et al., 2000
Tree bark			Pt: <9	Ma et al., 2001
	UK, Sheffield, London		Pt: ~9	
	Spain	Madrid, Tenerife	Pt: ~9	
	USA	San Francisco, Hawaii	Pt: 38	
	Japan	Tokyo, Yahushima	Pt: 38	
Pine needles	Palermo, Italy	Urban and rural areas	Pt: 1-102	Dongarrá et al., 2002
		(2000 June-July)	Pd: 1-45	

Grape culture		1991 vegetation		Alt et al., 1997
(soil)		near high traffic roads/(traffic free field-paths)	Pt: 0.84 (0.30)	
leaf			Pt: 0.33 (0.10)	
stalk			Pt: 0.13 (0.05)	
berry			Pt: 0.009 (0.002)	
(wine)			Pt: 0.0004 (0.0001)	
Grass	Dormund, Germany	city and its vicinity	Pt: 0.14-0.29	Alt et al., 1997
Potatoe		(peeled)	Pt: 0.10	
Carrot			Pt: 0.31	
Cabbage			Pt: 1.1	
Lettuce			Pt: 2.1	
Celery			Pt: 1.3	
Onion		(peeled)	Pt: 0.03	
Spruce shoot	Jülich, Germany		Pt: 0.55 Rh: 0.022	León et al., 1997

Table 12 PGM concentrations in the water ecosystem

Samples	Location	Other parameters	Concentration	References
Seawater	Pacific Ocean	-	Pd: 40 pg l ⁻¹	Lee, 1983
	Pacific Ocean		Pt: 150 pg l ⁻¹	Goldberg et al., 1986
Seawater	Menai Straits	August 1986	Pt: 332 pg l ⁻¹	Van den Berg and Jacinto, 1988
	Indian Ocean	depth of 6 m (1986)	Pt: 37 pg l ⁻¹	
		depth of 2000 m (1986)	Pt: 154 pmol l ⁻¹	
Tap water	Liverpool		Pt: 58.5 pmol l ⁻¹	
River water	Germany	Rhein, Schwarzbach	Pd: 0.4 ng l ⁻¹	Eller et al., 1989
Seawater	Indian Ocean	below 500m depth	Pt: 74 pg kg ⁻¹	Jacinto and Van den Berg, 1989
Seawater	Indian Ocean	below 500m depth	Pt: 55 pg kg ⁻¹	Colodner et al., 1993
Pelagic sediment		1440-1442 cm	Ir: 2.1 ng g ⁻¹	
		1420-1422 cm	Ir: 1.5 ng g ⁻¹	
Pelagic sediment		1440-1442 cm	Ir: 1.9 ng g ⁻¹	Kyte et al., 1986
		1420-1422 cm	Ir: 1.5 ng g ⁻¹	
Seawater		unpolluted	Pt: 0.1-0.2 ng l ⁻¹	Bertine et al., 1996
			Rh: 0.04-0.1 ng l ⁻¹	
Drinking water	Germany		Pt: 0.1 ng l ⁻¹	Laschka and Nachtwey, 1993
Groundwater	Germany		Pt: 3-38 ng l ⁻¹	

Rainwater	Germany		Pt: 1.4-74.5 ng l ⁻¹	
River water	Germany		Pt: 0.22-0.64 ng l ⁻¹	
Surface water	Frankfurt	pH 5.8-6.7	Pt: 9-78 µg l ⁻¹	Zereini et al., 1997b
Run-off from roads	Germany		Pt: 15-1600 ng l ⁻¹ (mean: 117)	Laschka et al., 1996
Run-off from roads	Germany	at the end of rain periods	Pt: 2 ng l ⁻¹	
Communal sewage	Germany		Pt: 8.7-33.4	Laschka and Nachtwey, unpub.
Fresh-water	Canada	mineralized sites	Pt, Pd: <5 ng l ⁻¹	Hall and Pelchat, 1993
Rainwater	Germany		Pt, Pd: <5 ng l ⁻¹	Helmers et al., 1998
River sediment	Sweden	urban area	Pt: 4.8-15 ng g ⁻¹ Rh: 2.5ng g ⁻¹	Rauch et al., 1999
Seawater	Baltic Sea		Pt: 2.2 ng l ⁻¹	Laschka et al., 1996
Seawater	California coast	at the surface water at 4500m depth	Pt: 100 pg l ⁻¹ Pt: 250 pg l ⁻¹ Ir: 9x10 ⁻⁴ ppt	Hodge et al., 1986
Macro algae			Pt: range 0.1 ppb-1 ppm (from algae to nodules)	
Ocean sediments				
Manganese nodules			Ir: 7.4 ppb	
Manganese nodules	deep-sea		Pd: 3.7-11.4 ng g ⁻¹	Hodge et al., 1986
Sediment	three rivers	Göteborg	Pt: <0.5-2.2 ng g ⁻¹	Wei and Morrison, 1994a
	Mölndal river	Göteborg, 1998	Rh: 0.67 ng g ⁻¹ Pd: 13.9 ng g ⁻¹	Rauch et al., 2000a

Surface sediments	Boston Harbor	1987, 1993, 1996	Pt: 1.0 ng g ⁻¹ Pt: 4.2; 4.62; 3.75 ng g ⁻¹ Pd: 19.93; 3.24; 4.22 ng g ⁻¹	Tuit et al., 2000
River sediment	Massachusetts Bay Mölnadal river	Sweden, 1999	Pd ≈ Pt: 0.6 ng g ⁻¹ Pt: 53.9 ng g ⁻¹ (mean) Pd: 38.7 ng g ⁻¹ (mean) Rh: 9.4 ng g ⁻¹ (mean)	Moldovan et al., 2001
Sediment	Stour river	1999 June	Pt: <0.29-4.42 ng g ⁻¹ Pd: 0.08-5.71 Rh: <0.11-0.26 Ru: <0.15-3.73 Ir: <0.03-2.69	De Vos et al., 2002
Drinking water	England	-	Pt: 0.2 µg l ⁻¹	Wildner, 1996
Drinking water	Germany	sites far from traffic	Pt: 1.0x10 ⁻⁴ ng g ⁻¹	Alt et al., 1997
Well water			Pt: 4.0x10 ⁻⁶ ng g ⁻¹	
Fen water			Pt: 1.3x10 ⁻³ ng g ⁻¹	
Rainwater			Pt: 8.0-17x10 ⁻⁵ ng g ⁻¹	
Glacier water			Pt: 1.0x10 ⁻⁴ ng g ⁻¹	
European eels	Germany	exposed eel liver unexposed eel liver	Pd: 0.14-0.25 ng g ⁻¹ Pd: < 0.10 ng g ⁻¹	Sures et al., 2001

Table 13 PGM concentrations in biological matrices

Samples	Location	Other parameters	Concentration	References
<i>Urine</i> (concentration unit: ng per g creatinine, or in $\mu\text{g l}^{-1}$)				
	California	citizens	Pt: 0.49-1.8	Johnson et al., 1975
	Australia		Pt: 0.11 (median)	Nygren et al., 1990
	Lord Howe Isl. Sidney	citizens	Pt: 0.18 (median)	Vaughan and Florence, 1992
	Lord Howe Island	one adult male (4 days)	Pt: 0.76-1.07 $\mu\text{g day}^{-1}$	
	Germany	occupational exposure	Pt: 0.021-2.9	Messerschmidt et al., 1992a
	Germany	24 h sampling period	Pt: 0.0012-0.035	Schramel et al., 1995
	Belgium		Pt: 0.0078	Parent et al., 1996
	Germany		Pt: 0.001	Begerow and Dunemann, 1996
			Pd: 0.0095	
			Rh: 0.0117	
	Germany	21 unexposed persons	Pd: 0.033-0.22	Begerow et al., 1997a

		Pt: 0.00048-0.0077	
Germany	general population (unexposed)	Pd: <0.020-0.080 (mean: 0.039) Pt: <0.070	Begerow et al., 1997b
Germany	pharmacists	Pt: 23 ng g ⁻¹	Ensslin et al., 1997
Umea, Sweden		Pt: 0.126±0.092	Nygren and Lundgren, 1997
Rome, and outskirts	6-10 year-old school children	Pt: <0.0006-0.0014 (med.: 0.001) Pd: 0.0052-0.0148 (med.: 0.0095) Rh: 0.0068-0.0179 (med.: 0.0117)	Krächler et al., 1998
United Kingdom	7 precious metal workers 10 motorway maint. workers 5 of Imperial College staff	Pt: 210-1180 Pt: 22-135 Pt: 48-224	Farago et al., 1998
Germany	non-occupational exposure	Pt: 6.5 ng g ⁻¹ (mean)	Schierl, 2000
Rome, Italy	310 school children	Pt: 0.9±1.1 ng g ⁻¹ Pd: 7.5±5.4 ng g ⁻¹ Rh: 8.5±8.0 ng g ⁻¹	Caroli et al., 2001
Germany	general population occupationally exposed	Pd: <0.036 Pd: 0.08-3.4	Schuster et al., 2000

	Germany	general population	Pd: <0.0025	Messerschmidt et al., 2000
		occupationally exposed	Pd: 0.3-1.0	
	Germany	general population	Pd: <0.01-0.028	Philippeit and Angerer, 2001
		occupationally exposed	Pd: <0.01-2.5	
Scalp hair	Australia		Pt: 3.02 (median)	Nygren et al., 1990
Sweat			Pt: 0.02 (median)	
Saliva			Pt: 0.07 (median)	
Fingernails			Pt: 19.0 (median)	
Hair	Lord Howe Isl., Sidney	citizens	Pt: 3.84 ng g ⁻¹	Vaughan and Florence, 1992
Faeces	Lord Howe Island		Pt: 10.7 ng g ⁻¹	
		daily for one adult male	Pt: 0.61-0.73 µg day ⁻¹	
Autopsy tissues			Pt: 3-1460 ng g ⁻¹	Vandiver et al., 1975
Liver			Pt: 0.05-0.24 ng g ⁻¹	Zeisler and Greenberg, 1982
Serum			Pt: 0.0009 (mean)	Krächler et al., 1998
			Pd: 0.050 (mean)	
Neurological tissue			Pt: 24-1800 ng g ⁻¹	Screnci et al., 1998

Blood (concentrations in $\mu\text{g l}^{-1}$)

Australia		Pt: 0.1-2.8 (median: 0.6)	Nygren et al., 1990
Australia, Sidney	citizens	Pt: 0.56 (median)	Vaughan and Florence, 1992
Umea, Sweden	graduate nurses	Pt: 2.2±1.7	Nygren and Lundgren, 1997
	staff nurses	Pt: 3.8±4.0	
	pharmacists	Pt: 0.47±0.31	
	unexposed persons	Pt: 1.2±0.69	
Germany	non-exposed persons	Pt: 0.0003-0.0013 (mean: 0.0009) Pd: 0.032-0.078 (mean: 0.050) Ir: 0.0001-0.0004 (mean: 0.0003)	Begerow et al., 1997c
United Kingdom	precious metal workers	Pt: 0.152-0.423	Farago et al., 1998
	motorway maint. workers	Pt: 0.126-0.158	
	Imperial College staff	Pt: 0.115-0.139	

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