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Uptake of Platinum Group Metals in Raptor Feathers



Kristine Jensen

Abstract

Concentrations of the platinum group metals (PGMs) platinum, palladium and rhodium are increasing rapidly in the environment, especially since the introduction of autocatalysts in the late 1980's. This has caused some concern about the potential negative environmental impact of these metals. The aim of this study was to investigate uptake and levels of platinum, palladium and rhodium in Swedish raptors. Sparrowhawks, peregrine falcons and gyrfalcons from different parts of Sweden in different habitats and with different food choices were studied and compared. Raptors are on the top of food chains and therefore they are appropriate as study material. Inductively coupled plasma mass spectrometry (ICP-MS) after microwave digestion was used to determine uptake and levels of PGMs in raptor feathers and laser ablation-ICP-MS was used to investigate uptake and metabolism mechanisms of PGMs. An attempt has also been made to determine the bioaccumulation potential of PGMs.

Mean concentrations of platinum, palladium and rhodium in feathers from peregrine falcon, sparrowhawk and gyrfalcon ranged between 0.2 and 6.4 ng/g, 0.4 and 16.6 ng/g and 0.2 and 8.6 ng/g, respectively. Sparrowhawks had significantly higher Pd and Rh levels than captive peregrine falcons. The background level of platinum, palladium and rhodium in raptors was estimated to around 0.2, 0.4 and 0.2 ng/g respectively. Results suggest that PGM levels have increased by approximately 10 times in wild peregrine falcons since 1976. LA-ICP-MS results suggest that platinum group metals are generally transported relatively quickly from the blood, within approximately one hour. However, possible evidence for PGMs in blood was found only in a few urban sparrowhawks. Results also suggest that rhodium and especially palladium are more mobile in the environment than Pt, which is suggested not to bioaccumulate. No biomethylation of PGMs seems to occur in raptors.

Keywords: Raptors, platinum group metals, platinum, palladium, rhodium, autocatalyst, LA-ICP-MS, bioavailability, bioaccumulation, microwave digestion.

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1. Introduction

Concentrations of the platinum group metals (PGMs) are increasing rapidly in the environment, but to which extent is yet incompletely known. The major source of these metals is believed to be autocatalysts, from which PGMs are emitted due to surface abrasion. The PGMs emitted are bound to particles of aluminium oxide in the μm size range. The particles emitted are in a metallic form, which is relatively immobile in the environment. However, in spite of the reduced CO, HC and NO_x emissions thanks to the autocatalyst, it is simply an "end-of-the-pipe" technique and typical for this kind of technique is that it has drawbacks, in this case emission of PGMs. Helmers (1997) says "Although less than 80 % of the cars in Germany were equipped with catalyst in 1997, and although PGMs have been emitted for not more than 10 years, in relevant quantities, levels of Pt in road dust already touch the magnitude of Pt-rich ores".

Recent studies have shown that platinum group metals are not as inert in the environment as previously assumed. Therefore, there is now a growing concern over the potential negative environmental impact of these metals. This has motivated extensive research on PGMs in the last decade. Platinum has been investigated rather thoroughly, while little is yet known about palladium and rhodium. There is also a lack of knowledge about transformation and pathways of PGMs in the environment and their potential bioaccumulation in organisms.

This report focuses on the determination of platinum, palladium and rhodium in the feathers of three raptor species in Sweden; sparrowhawk, peregrine falcon and gyrfalcon. The possible bioaccumulation of PGMs in raptors is also examined. The report starts with some background information on the biology and ecology of the birds studied, on other metals in birds and feathers in general and on chemical and physical properties of PGMs. This is followed by a survey of the distribution of PGMs in the environment, from use and occurrence to concentrations in different environmental compartments and biological materials such as air, soil, road dust, runoff water, plants, animals and humans. Detailed descriptions of the autocatalyst function and emissions of PGMs are also included. The analytical techniques for PGM analysis are reviewed and the methods for sample analysis are described. The

study finishes with results and discussion of the results, conclusions and some suggestions for further studies.

2. Aim

The main goal with this study is to examine how and to which extent PGMs (Pt, Pd, Rh), mainly Pt, are taken up by raptors. This will be accomplished by:

- Analysing PGMs in feathers using two different techniques; ICP-MS after microwave digestion and LA-ICP-MS.
- Comparing PGM levels in feathers from birds in different populations; sparrowhawks, gyrfalcons, peregrine falcons and their prey species.
- Studying variations of PGM concentrations with time in raptor feathers.

Examples of uptake mechanisms are ingestion of body-contaminated prey, preening, inhalation of airborne particles or ingestion of prey that has superficially contaminated feathers or fur. Prey will be examined to investigate the level of contamination in the food of the raptors. Studies on uptake mechanisms will also help in the investigation of possible bioaccumulation of PGMs in raptors.

The secondary goal was to gain background knowledge on PGMs and their analysis; extent of emissions, concentrations, behaviour and effects in the environment and the instrumentation used for analysis.

3. Hypothesis

It is expected that urban raptors such as the sparrowhawk, living and hunting close to major roads and urban areas, have higher levels of platinum group metals in their body compared to rural raptors such as the gyrfalcon and the peregrine falcon, living in the countryside. A common prey species of the sparrowhawk is the house sparrow (*Passer Domesticus*). Since the sparrow lives in the direct vicinity of urbanisation and takes dust-baths in road dust and drinks water from polluted gullypots, it is believed to contain relatively high amounts of PGMs. It is likely that the dust-bathing causes dust particles containing PGMs to attach to the vane of their feathers, which would be reflected in analyses of intact sparrow feathers. The main cause of the expected elevated levels of PGMs in urban raptors as compared to countryside raptors is the ingestion of more contaminated food. Pollution of PGMs in air, inhaled by raptors, is expected to contribute less.

It is also expected that the non-migratory gyrfalcon, which lives in a mountain area in the north of Sweden, exhibit significantly lower levels of PGMs than other raptors. The main prey of the gyrfalcon, the willow-grouse (*Lagopus Lagopus*), is also expected to have very low levels of PGMs, probably even lower than the gyrfalcon.

It is further expected that feathers from raptors before 1986, when catalysts were introduced in Europe, contain lower levels of PGMs than younger raptors. It is also hypothesised that peregrine falcons from northern Sweden might have somewhat higher concentrations of PGMs than peregrine falcons from southern Sweden, since they are on top of an aquatic food chain while southern peregrine falcon are on top of a terrestrial food chain. Captive falcons are believed to contain smaller amounts of PGMs than sparrowhawks and wild peregrine falcons, due to a controlled diet and breeding in captivity.

There is also a theory that solubilisation of PGMs released from autocatalysts into the environment results in bioaccumulation through metallothionein/methylation pathways and subsequently elevated concentrations in exposed raptors. This theory will be evaluated in a first attempt in this study.

4. Biology and ecology of the raptors studied

The raptors examined in this study were sparrowhawk (SH), peregrine falcon (PF) and gyrfalcon (GF). The sparrowhawks come from the area around Gothenburg in south-western Sweden, some from more urban places and some from more rural areas and two individuals come from the countryside in Norway. The peregrine falcons come from northern Sweden (Norrbotten), south-western Sweden (Bohuslän, Dalsland, Västergötland), captivity, one bird is from 1982 (Halland) and another from 1976 (Scotland), before catalysts were used. The captive falcons are kept at a breeding station outside Gothenburg. The gyrfalcons all come from northern Sweden (Norrbotten). Their main prey species, the grouse, comes from Lappland and Västerbotten in northern Sweden. For geographical orientation, see figure 1.

Figure 1. Map of Sweden.

4.1 The sparrowhawk

The sparrowhawk (*Accipiter nisus*) is a relatively small raptor with rather short, wide and blunt wings and a long tail (figure 2). The total length of the bird from the beak to the tail is 30-40 cm. The wingspan is around 60-80 cm. The sparrowhawk shows reversed dimorphism, i.e. the female is larger than the male (Mullarney *et al*., 1999).

Figure 2. The sparrowhawk.

The sparrowhawk is spread all over Europe and the western part of Russia. In 1984, the estimated population size was 60.000-90.000 pairs of sparrowhawks in Europe. In the 1950-60's, the population decreased around 60-90 % due to eggshell thinning which was caused by the pesticide DDT. Illegal perching and hunting was also common up until the middle of the 1980's (Génsböl, 1984).

The habitat of the sparrowhawk is an open landscape with areas of mixed or coniferous forest. They place their nest preferentially in old trees, 5-8 metres above the ground. Sparrowhawks also nest in cities. In wintertime, even sparrowhawks in the countryside hunt to a greater extent closer to cities, since small birds gather at the feeding places arranged by humans. The adult sparrowhawks in the vicinity of Gothenburg are resident also during winter, while juveniles migrate (Génsböl, 1984).

The food chain of the sparrowhawk in the area of Gothenburg may look like the one in figure 3. The main part of the diet (98%) is small birds such as sparrows, chaffinch, tits, thrushes etc. The rest of the diet consists of small mammals, mostly different species of voles (Génsböl, 1984).

The sparrowhawk moults in the summer. Most females start around egglaying in May, while males start around hatching in June. The moult takes about 4 months (Newton, 1986). During the moult, new feathers are formed, and old feathers are shed. About 45-50 days are required for the formation of a feather.

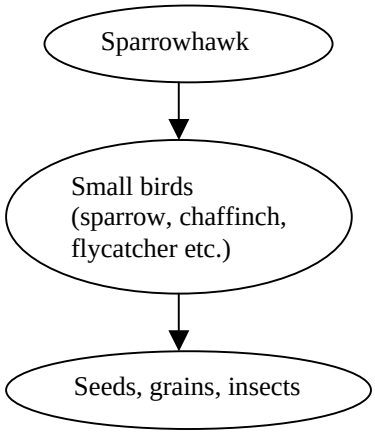


Figure 3. Food chain of the sparrowhawk in the Gothenburg area.

4.2 The peregrine falcon

The peregrine falcon (*Falco peregrinus*) is a falcon of average size; the length from the tail to the beak is 40-50 cm and the wingspan is around 90-110 cm (figure 4). The wings are pointed. The peregrine falcon also shows reversed dimorphism (Mullarney *et al*., 1999).

Figure 4. The peregrine falcon.

During the 1950-60's, the peregrine falcon population declined rapidly due to pesticides such as DDT, PCB, aldrin and dieldrin. The maximum population in Sweden before the decline was 900-1400 pairs, spread over all of Sweden. In 1970, the lowest number was recorded; 15 pairs in Sweden. In the 1980's, the negative trend was stopped. In 1994, there were around 60 pairs in Sweden. Today, there are two groups of peregrine falcons in Sweden, one group in the north (Norrbotten) and one in the south-west (Halland, Bohuslän, Dalsland) (Lindberg, 1996a).

The nest is almost always placed on steep cliffs, but in Norrbotten the nest is also sometimes placed on the large bogs. The peregrine falcon accepts most types of surroundings, even areas with a rather extensive human activity, as long as their nest is undisturbed. They often return to the same nest year after year (Lindberg, 1996a).

The Swedish falcons are predominantly migratory birds, and they leave their breeding grounds in August-September. They migrate mostly to England, Holland, Germany, Belgium and France. Observations indicate that falcons from northern Sweden migrate further south than the falcons in south-western Sweden. They return to Sweden in March-April (Lindberg, 1996a).

The food choice of the peregrine falcon differs between the two groups in Sweden. In south-western Sweden, the most common species include gulls, pigeons, terns, blackbirds, jackdaws etc. In northern Sweden, the main food choice is waders, ducks and black-headed gulls. The food chain is terrestrial in south-western Sweden while it is aquatic in northern Sweden (Lindberg, 1996a). The prey species of the wild peregrines migrate to western central Europe during winter. The diet of the captive peregrine falcons is captive chickens that are bred up at the same breeding station as the peregrine falcons. Examples of food chains for the peregrine falcon are shown in figure 5.

The female peregrine falcon moults from May to September. The male starts and finishes one month later. A new feather is formed during 45-50 days.

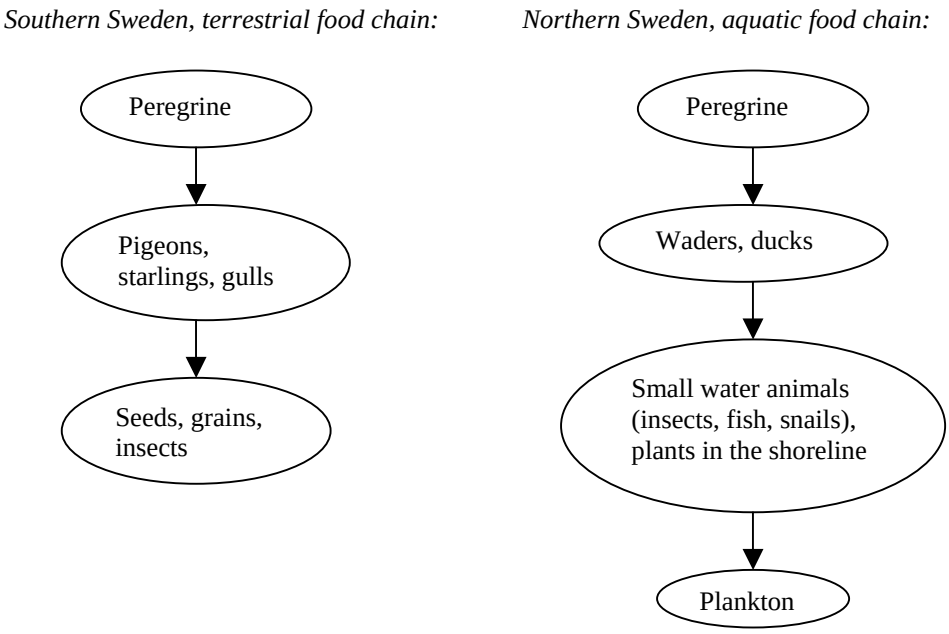


Figure 5. Food chain of the peregrine falcon.

4.3 The gyrfalcon

The gyrfalcon (*Falco rusticolus*) is the largest falcon; the length from the tail to the beak is 53-63 cm and the wingspan is around 110-130 cm (figure 6). The wings are wide and rather blunt. The gyrfalcon also shows reversed dimorphism.

Figure 6. The gyrfalcon.

The gyrfalcon is spread circumpolar in the arctic and northern temperate zones. The world population is 7000-17000 pairs. In Sweden, the gyrfalcon

can be found in the mountain range from Dalarna and further north. The population of gyrfalcons in Sweden is probably relatively stable and has a good reproduction. There were 100-200 pairs living in Sweden in 1992. However, the size of the population varies with the access to grouse, since it is the gyrfalcon's staple food (Lindberg, 1996b).

The gyrfalcon in northern Sweden does not migrate.

Their habitat is the open, arctic landscape. They can be found on the tundra, on cliffs at the coast and in mountain areas. They breed on steep cliffs in the birch- and willow-zone in the mountain range.

An illustration of the food chain is presented in figure 7. The grouse is the major food choice of the gyrfalcon; it makes up 83 % of their total food. However, during bad grouse-years, the gyrfalcon will feed on more waders, ducks, thrushes and small mammals like lemmings, voles and weasels. During the winter the only alternative is the grouse. The food chain is predominantly terrestrial, but when the gyrfalcon choose waders and ducks instead of grouse, it becomes part of an aquatic food chain. The gyrfalcon has been very little affected by pesticides, since the grouse is herbivorous and does not migrate (Lindberg, 1996b).

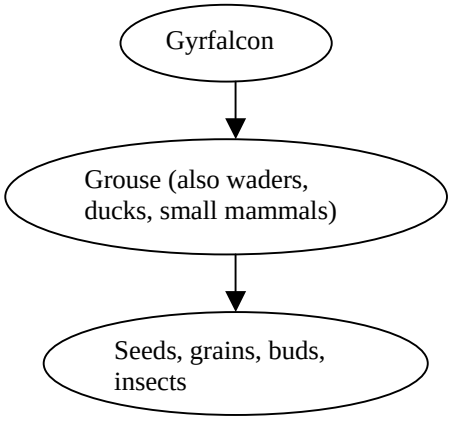


Figure 7. Food chain of the gyrfalcon.

The female gyrfalcon moults from May to September. The male starts and finishes one month later. It takes 45-50 days to form a new feather.

5. Metals in birds

This chapter describes the behaviour of metals in birds, with emphasis on mercury, lead and cadmium, in order to find a possible similar behaviour of PGMs in birds.

The degree of metal exposure to raptors and metalloids depends largely on the amounts transferred via the diet, and food choice is important in how extensive the uptake of metals is in the birds. Raptors on top of aquatic food chains generally have higher levels of metals than raptors on top of terrestrial food chains. That is partly due to that aquatic organisms also take up toxins via gills and/or skin in the water (Jönsson *et al.*, 1995; Lindberg, 1983). Heavy metals tend to be held in one particular tissue at much higher levels than in others, for example in liver, kidneys or feathers (Furness and Greenwood, 1993).

Metals in birds are measured in different ways; by analysing feathers, internal organs such as liver and kidneys, muscles, blood, eggs or faeces. There are several advantages of using feathers as bioindicators of metal exposure, for example: 1) collecting feathers is non-invasive and therefore particularly useful for endangered species, 2) feather metal levels correlate roughly with internal levels, 3) feathers reflect blood levels during the time of feather formation and blood reflects present or very recent exposure, 4) metal levels in feathers are stable compared to levels in soft tissues, 5) feathers are easy to collect and store for long periods of time and 6) wing feathers can provide time sequence exposure data in the limits of a few weeks rather than over long periods of time as in internal tissues (Solonen *et al*., 1999; Burger and Gochfeld, 1997).

Feathers are epidermal structures of keratin. Feathers do not grow like trees, but like hair. The tip of the feather shaft forms first and the inner parts of the feather shaft are formed sequentially until the structure is complete. During feather growth, the shaft contains an axial artery that eventually will cease functioning as the feather is being completed. When fully formed, the blood flow through the artery is completely stopped. To be noted is that blood levels of metals reflect current exposure as well as metals mobilised from other internal tissues. The formation of one raptor feather takes about 45-50 days, and all feathers are replaced in approximately 4 months (the moult period). Keratin is rich in amino acids, which contain sulphur hydryl groups (-SH) that form disulfide bonds with heavy metals in the blood. Therefore, many heavy metals, particularly mercury, are sequestered in growing feathers and eventually shed. Thus, feathers serve an important excretory role (Burger and Gochfeld, 1997).

A study on metal concentrations (Al, Cd, Pb, Zn, Cu) in bird feathers showed a relatively high variability both within and between species, especially in wild populations. In raptors, variations in metal concentrations were generally highest in vole-eaters, intermediate in bird-eaters, and smallest in fish-eaters. The largest variations were found for aluminium, cadmium and lead, while they were smaller for zinc and copper (Solonen *et al*., 1999). Differences in metal levels between sexes are relatively small, but they are generally higher in adult than juvenile birds (Furness and Greenwood, 1993).

5.1 Mercury

Bird species feeding on fish have higher levels of mercury than species that eat terrestrial small mammals, insects and seeds. A study showed higher mercury levels in peregrine falcons living in the north of Sweden than in peregrines living in southern Sweden. That is because northern peregrines are the top predators in an aquatic food chain, while southern peregrines are on top of a terrestrial food chain (Lindberg, 1983; Burger and Gochfeld, 1997).

Feathers is the main excretory pathway of mercury. On average, mercury in feathers accounts for 60 to 93 % of the total body burden in adult birds and 48 to 91 % in fledglings. Almost 100 % of the mercury in feathers is methyl mercury (Burger and Gochfeld, 1997). In seabirds, however, mercury excretion by moulting is negligible and they do not have high mercury levels in their feathers. It has been suggested that seabirds rather can control mercury accumulation by demethylation metabolism in enzyme systems, mainly in the liver, but also in muscle and kidneys. Methyl mercury is transformed to inorganic mercury. The inorganic mercury is stored as an immobilisable form in the liver, which leads to high levels (97-98 %) of inorganic mercury in the liver. (Kim *et al*., 1996). Also in raptors, demethylation of methyl mercury seems to be a significant detoxification route (Burger and Gochfeld, 1997).

It is possible to estimate mercury levels in internal tissues if the feather concentration is known. Several authors have claimed a ratio of 7:3:1 for mercury levels in feathers, liver and muscle, respectively (Lewis *et al.*, 1993).

A study by Lewis *et al.* (1993) showed significantly higher mercury levels in primary feathers from male compared to female herring gulls. It was also estimated that female gulls may excrete over 20 % more mercury via their eggs than could be excreted by male birds.

5.2 Lead

Metallic lead (from lead ammunition) in soil is gradually eroded to become bioavailable to organisms, such as earthworms. Uptake and accumulation of lead from soil by earthworms depends on the physical and chemical properties of the soil, on the earthworm species and the level of contamination. That is the way birds feeding on earthworms will be contaminated by lead. Another route of exposure is through extensive preening of their plumage, since lead may be deposited as dust on feathers. Significantly higher lead levels have also been found in bird species higher on the food chain feeding on fish or other large vertebrates compared to species lower on the food chain feeding on vegetation and small insects (Burger, 1995). Lead damages the hematopoietic, nervous, skeletal and excretory systems (Burger, 1995; Vyas *et al*., 2000). In blood, lead is primarily bound to red blood cells. It inhibits enzymes, such as ALAD. Lead accumulates in the skeleton and in internal organs (Folkesson, 1976). Effects in birds include delayed egglaying, decreases in clutch and egg size, mortality of embryos and nestlings, depression of growth and altered behaviour that affects survival. Little is yet known about the dynamics of lead in birds' bodies (Burger, 1995). However, lead in feathers has not been shown to relate to lead exposure, it rather seems like blood levels is a more accurate measure of lead exposure to birds (Pain *et al*., 1993).

5.3 Cadmium

Cadmium accumulates primarily in liver and kidneys (Jönsson *et al*., 1995). It slows growth rate and development in a number of organisms, also birds. A study showed that especially the cadmium that was bound in feathers was strongly correlated with lowered growth rates in heron chicks. It has also been found that cadmium levels in heron tissues increase with age, indicating that the birds bioaccumulate the metal (Spahn and Sherry, 1999).

6. Chemical and physical properties of PGMs

The metals belonging to the platinum group are platinum, palladium, rhodium, iridium, ruthenium and osmium. In this study, PGMs refers to the metals platinum, palladium and rhodium. The chemical properties of platinum, palladium and rhodium are in many cases similar. Common properties include high catalytic activity, resistance to corrosion and a strong tendency to form complexes. They also have high melting and boiling points, around 1600-2000°C and 3100-4100°C respectively. The chemical resistance of PGMs to different reagents (acids etc.) is highest for Rh and lowest for Pd (Habashi, 1997).

6.1 Platinum

Platinum is a relatively soft and silvery metal with the atomic number 78 and atomic weight 195.09. Platinum occurs mainly as the isotopes ^{194}Pt (32.9 %), ^{195}Pt (33.7 %) and ^{196}Pt (25.4 %). Platinum is considered relatively inert, but when subjected to temperatures above 450 °C (which is common in catalysts), the volatile oxide PtO_2 is formed. Halogens, sulphur and molten sulphur compounds, cyanides, heavy metals and hydroxides can also affect platinum. The principal oxidation states are +2, +4 and 0, the most common being +2. The +4 oxidation state is the most stable one.

Platinum has a strong tendency to form complexes with other compounds. It binds to a large number of ligands (ions or neutral molecules) to form neutral or charged complexes or salts. The geometric arrangement of the complex determines its reaction characteristics and is very important in biochemical processes (Lindell, 1997).

The metal platinum and platinum oxides are insoluble, but the complex salts are soluble in water to different degrees, as shown in Table 1. The solubility is important for the toxicity of the compound. A water-soluble platinum compound is more toxic than an insoluble one.

Table 1. Solubility in water for some platinum compounds. Adapted from Lindell, 1997.

Chemical name	Solubility in water
Platinum	Insoluble
Platinum(II)oxide	Insoluble
Platinum(IV)oxide	Insoluble
Platinum(II)sulphide	Insoluble
Platinum(IV)sulphide	Insoluble
Platinum(II)chloride	Insoluble
Platinum(IV)chloride	Slightly soluble
Platinum(IV)chloride (pentahydrate)	Soluble
Platinum(IV)sulphate (tetrahydrate)	Soluble
Hexachloroplatinic(IV)acid (hexahydrate)	Very soluble
Ammonium tetrachloroplatinate(IV)	Soluble
Ammonium hexachloroplatinate(IV)	Slightly soluble
Potassium tetrachloroplatinate(II)	Soluble
Potassium hexachloroplatinate(IV)	Slightly soluble
Sodium hexachloroplatinate(IV)	Very soluble

6.2 Palladium

Palladium is also a soft and silvery metal. It has the atomic number 46 and the atomic weight 106.4. Palladium occurs as the isotopes ^{105}Pd (22.3 %), ^{106}Pd (27.3 %) and ^{108}Pd (26.5 %). The principal oxidation state is +2. Palladium is more reactive than platinum; it is for example more easily dissolved in acids. It also reacts more readily with halogens and oxygen (Habashi, 1997).

6.3 Rhodium

Rhodium is a ductile and silvery metal, as the other platinum group metals. Rhodium has the atomic number 45 in the periodic system and there is only one isotope, ^{103}Rh. The atomic weight is 102.9. The principal oxidation states for rhodium are +1 and +3. Rhodium is relatively inert, but it reacts with oxygen and halogens at high temperatures (Habashi, 1997).

7. Distribution of PGMs in the environment

7.1 Occurrence and use

The platinum group metals are widely spread but rare metals. They are concentrated in the Earth's core and mantle and the abundance in the Earth's crust is low. The Earth's crust contains around 0.05-0.4 ng/g of PGMs (Helmers and Kümmerer, 1997). Platinum makes up about 5 x 10^{-7} % of the Earth's crust (Lindell, 1997). Palladium and rhodium have abundances in the Earth's crust of about 1 x 10^{-7} %.

Platinum group metals are deposited in primary deposits such as ores and in secondary deposits like alluvial material. They occur in a large number of minerals, such as sperrylite ($PtAs_2$), cooperite (PtS), stibiopalladinite (Pd_3Sb) and ferroplatinum (Fe-Pt). PGMs are often found in combinations with metals like nickel, cobalt and copper minerals. The largest PGM deposits have been found in South Africa (72 %), south-western USA (12 %) and in Ural and Siberia in Russia (10 %) (Habashi, 1997). Platinum and palladium alone constitute around 90 % of the world's PGM mining production (Helmers and Kümmerer, 1997).

Platinum is mainly used in three-way catalysts, jewellery, as an anti-tumour drug in medicine (*cis*-platin), in catalysts in the chemical industry and it is often alloyed with other metals and used in electronics and dentistry (Lindell, 1997). The principal uses of palladium are in electronics, electrical industries, circuitry, dental alloys and in autocatalysts. Rhodium is mainly used with platinum in autocatalysts and in catalysts in the chemical industry (Cotton, 1997).

As shown in figure 8, the total output of platinum in the world has increased over the last decades. Since 1960, there has been a four-fold increase in the annual platinum world output (Habashi, 1997). Between 1986 and 1995, the industrial demand for platinum, palladium and rhodium increased by 66 %, 110 % and 71 % respectively (Helmers and Kümmerer, 1997).

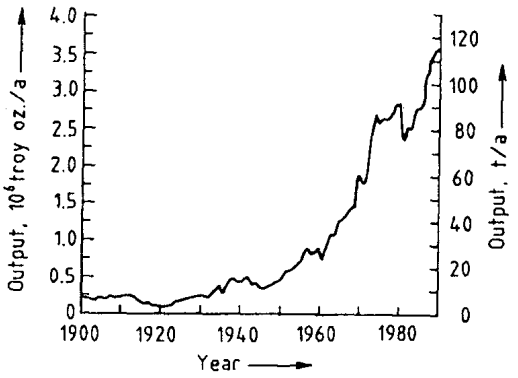


Figure 8. The history of world platinum ouput. (Habashi, 1997)

The demand for platinum, palladium and rhodium for production of autocatalysts world-wide amounts to more than 1/3 of the annual production of platinum and palladium and more than 4/5 of the annual production of rhodium (Habashi, 1997). 17 tonnes of the 28 tonnes of platinum sold in the world was used for the production of autocatalysts in 1993 (Artelt *et al.*, 1999). The use of palladium in three-way catalysts is now starting to increase, since palladium has similar catalytic properties as platinum and is much cheaper. Palladium replaces or reduces the amount of platinum in the catalyst (Rauch *et al.*, 1999c). The palladium demand of the European autocatalyst industry doubled from 1994 to 1995 (Johnson Matthey, 1996).

However, autocatalysts is not the single source of PGMs. PGM-processing industries emit PGMs in a more widespread distribution. Smaller amounts of Pt is also used in anti-tumour treatment. This Pt is then excreted by patients and discharged into the wastewater, and it is probably in a biologically available form (Helmers and Kümmerer, 1997).

7.1.1 Three-way catalysts

The first noble metal car catalysts were developed in order to meet the strict emission regulations in the USA in the early 1970's. All new cars have been equipped with catalytic converters since 1975 in the USA and since 1986 in Europe. (Palacios *et al.*, 1999) Since 1993, autocatalysts are mandatory on all new cars in Europe (Rauch *et al*., 1999c).

Three-way catalysts (TWCs) are car catalysts that can reduce the three compounds carbon monoxide (CO), hydrocarbons (C_xH_y) and nitrogen oxides (NO_x). Platinum and palladium are used to oxidise carbon monoxide and hydrocarbons to carbon dioxide and water, while rhodium reduces nitrogen oxides, primarily to N_2. Thus, a three-way catalyst consists of Pt/Rh, Pd/Rh or Pt/Pd/Rh. Three-way catalysts usually consist of a front substrate containing Pt and Rh and a rear substrate containing Pd and Rh. The main advantage with these three metals is that they have a significant catalytic activity even at low temperatures (220 °C). (Palacios *et al.*, 1999)

The main reactions that take place in the autocatalyst are:

Oxidation reactions

$$CO + ½\ O_2 \rightarrow CO_2$$

$$H_2 + ½\ O_2 \rightarrow H_2O$$

$$C_xH_y + (x+y/4)O_2 \rightarrow xCO_2 + y/2\ H_2O \qquad (1)$$

Steam reforming

$$C_xH_y + xH_2O \rightarrow xCO + (x+y/2)H_2$$

NO_x reduction

$$2\ CO + 2\ NO \rightarrow 2\ CO_2 + N_2$$

$$C_xH_y + (2x+y/2)NO \rightarrow xCO_2 + y/2\ H_2O + (x+y/4)N_2 \qquad (2)$$

$$H_2 + NO \rightarrow H_2O + ½\ N_2$$

Water-gas shift

$$CO + H_2O \rightarrow CO_2 + H_2$$

Platinum is active in the water-gas shift and it is also an oxidation catalyst for carbon monoxide and hydrocarbons. Rhodium is active in the steam reforming reaction and it can favour nitric oxide reduction by hydrocarbons (reaction (1) and (2)). (Palacios *et al.*, 1999)

The catalyst is held in a metal can which is placed in the exhaust stream system. It consists of a ceramic honeycomb of cordierite ($2MgO•2Al_2O_3•5SiO_2$) with a cell density of about 400 cells/cm^2. The cordierite walls are coated with a washcoat in which the active noble metals are dispersed. The washcoat consists of about 90 % γ-Al_2O_3 (alumina) and a mixture of metals and/or their oxides, such as Ce, Zr, Ba, Y, Ni etc. Figures 9 and 10 show the structure of the monolith catalyst.

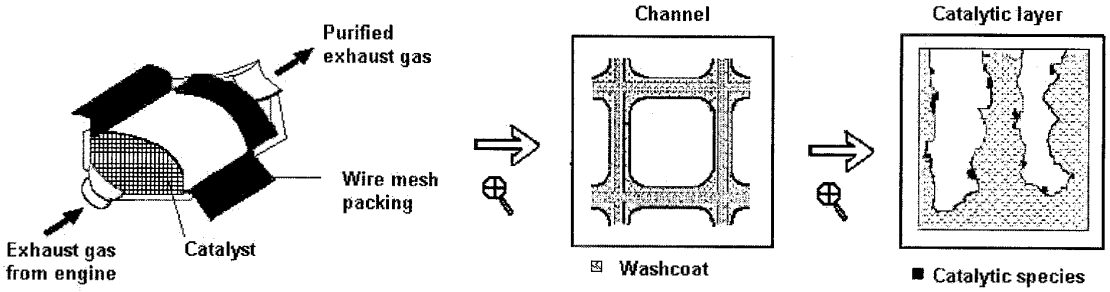


Figure 9. Structure of the monolith catalyst (Janssen and van Santen, 1999).

TWCs contain 0.10-0.15 % w/w of the noble metals Pt, Pd and Rh, where platinum is the most abundant. A TWC contains ca. 2 g of PGMs (Habashi, 1997). In Europe, the Pt/Rh ratio in the autocatalyst is around 5. The Pt/Pd ratio was around 1.7 in 1986, but it is now changing towards lower values, since platinum is being replaced by palladium (Tuit *et al.*, 2000; Palacios *et al.*, 1999).

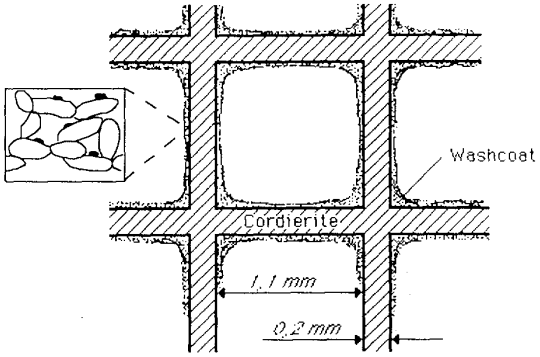


Figure 10. Cross-section of a catalyst with 62 cells/cm^2. The small picture of the washcoat layer shows the oxide support (white) and the precious metal particles (black). (Stenbom, 1999)

Platinum in the fresh autocatalyst is not only present in a metallic form, but also as oxides, chlorides and bound to hydrocarbons. Rhodium is present in a metallic form and as an oxide. (Rauch *et al.*, 1999c)

The two main factors for maximum conversion efficiency of the three contaminants (hydrocarbons, nitrogen oxides and carbon monoxide) are firstly the catalyst type and structure and secondly the air-fuel ratio, which should

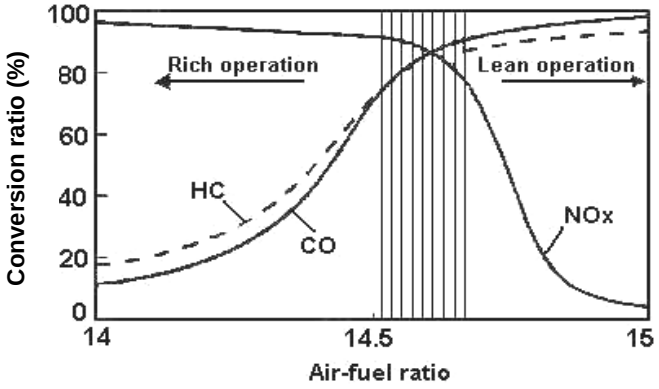


Figure 11. Pollutant conversion rates as a function of variations in the air-fuel ratio (Holmgren, 1998).

be around 14.6 (figure 11). At maximum efficiency, the catalyst can reduce CO, HC and NO_x emissions by 90 % (Palacios *et al.*, 1999). The temperature is also a very important factor. The light-off temperature in the catalyst, i.e. the temperature where the conversion ratio is 50 %, is 220 °C.

The catalyst temperature is typically around 600 °C, but in cases of engine misfiring it can rise higher than 850 °C. At high temperatures and under oxidising conditions, rhodium and palladium can be oxidised to Rh_2O_3 and PdO, respectively. Pt-Rh and Pd-Rh alloys can also be formed. In addition, rhodium starts to penetrate the alumina washcoat at temperatures above 600 °C, leading to a drastic decrease of the NO_x reduction (Palacios *et al.*, 1999). Other studies showed that if the ignition of one of the four cylinders is disconnected, platinum emissions increase by a factor of 100. If the temperature rises due to continuous ignition interruptions, platinum emissions may increase by a factor of 1000. Even after a return to normal ignition conditions, platinum emissions remain about 10 times higher than before (Helmers, 1997).

There are two main strategies for evaluating the amount of PGMs released into the environment by the autocatalyst. The first is to measure the PGM content directly in the exhaust fumes and the second is to determine the amount of PGMs in environmental materials such as soil, water, airborne particles, plants, animals etc. and from that calculate the PGMs emitted. Data on platinum emission rates from autocatalysts varies over four orders of magnitude. The largest difference occurs between results from test stand experiments, which are very low, and results derived from environmental investigations.

Helmers (1997) evaluated all data available on the platinum emission rate from different studies by a mathematical model. He found that a realistic emission rate under real driving conditions should be around 0.5-0.8 μg/km, taking the factor of uncertainty of the different studies into account.

König (1992) calculated the emissions of platinum from autocatalysts to ca. 2 ng/km at a speed of 60 km/h and ca. 40 ng/km at a speed of 140 km/h. The emission rate is illustrated in figure 12. In figure 12, the data of König (circles) has been mathematically extrapolated by Helmers (1997) and it shows that Pt emissions may be 10 times higher when doubling the speed from 100 to 200 km/h.

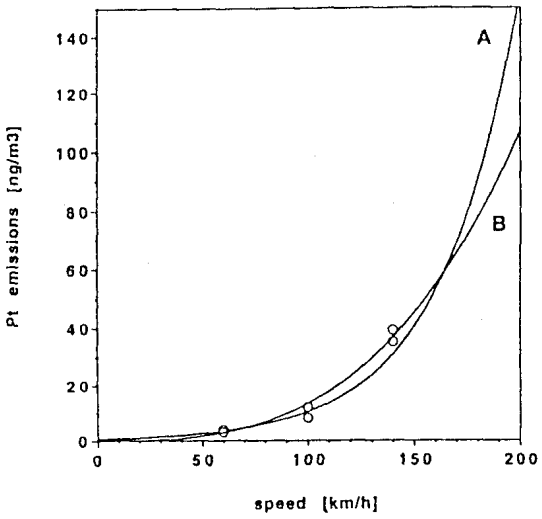


Figure 12. Platinum emissions from auto-catalysts as a function of car speed (Helmers, 1997).

Zereini (1999) suggested that PGM emissions from autocatalysts are dependent on acceleration and speed. Significantly higher PGM values were found along an accelerating road compared to an exit road from a highway in Germany. Moreover, simulated city driving yielded 2-3 times more PGM emissions compared to driving at constant speed.

Modern monolith (honeycomb, three-way) catalysts emit in the order of 2 magnitudes less PGMs than the older, pelleted ones. The pellet oxide catalyst consists of aluminium pellets coated with PGMs through which the exhaust gas passes. Pellet type catalysts are no longer in use in the U.S. and they have never been used in Europe (König *et al*., 1992).

A recent study by Artelt (1999) showed that the mean emissions of platinum in test stand experiments reached about 90 ng/km at a speed of 130 km/h. Mean concentrations of platinum in the exhaust gas in test-stand experiments ranged from 3.3 to 39.0 ng/m^3 for particles with an aerodynamic diameter >5 μm in a study by König (1992). Cubelic (1997) determined platinum emissions under real driving conditions to at least 150 ng/km. Schäfer (1998) determined a mean platinum emission rate to 270 ng/km under real driving conditions. Helmers (1997) determined platinum emissions from automobile sources other than the autocatalyst (fuel, tires and brake pads) and found that they were 1-6 orders of magnitudes lower than the autocatalyst emissions.

Moldovan (1999) measured PGM emissions from an aged catalyst (18000 km) at a constant speed of 80 km/h and Pt, Pd and Rh emissions ranged between 6.3-7.5, 1.2-1.9 and 0.6-1.2 ng/km respectively. When simulating a driving cycle of different speeds, emissions were increased (11-58, 2-24 and 1.5-7 ng/km for Pt, Pd and Rh respectively). A more recent study determined Pt, Pd and Rh emissions from aged (30000 km) three-way catalysts to 6-11, 9-58 and 3-11 ng/km respectively (Palacios *et al*., 2000). It was also found in this study that PGM emissions were significantly higher in a fresh catalyst compared to an aged one. The Pt, Pd and Rh emissions from a fresh catalyst were around 100, 250 and 50 ng/km. Another study calculated the palladium emissions from autocatalysts in Boston, USA, based on traffic intensities and sediment concentrations, and they ranged between 4.0 and 6.4 μg/km (Tuit *et al*., 2000). However, the estimated palladium emissions calculated by Tuit (2000) is based on very rough calculations using Helmers (1997) high emission rates, which included a lot of assumptions.

From the PGM emission values determined by Moldovan (1999), Pt/Pd and Pt/Rh ratios in the exhaust gas can be calculated. The Pt/Pd ratio was 2.4-5.5 and the Pt/Rh ratio was 7.3-8.3. So, PGMs are emitted from catalysts in the following decreasing order: platinum > palladium > rhodium. Ratios can also be calculated from the emission rates determined by Palacios *et al.* (2000). The Pt/Pd ratio was 0.2-0.7 and the Pt/Rh ratio was 1-2. So, according to this study, PGMs are emitted from autocatalysts

in the order palladium > platinum > rhodium. Since autocatalysts are the major source of PGMs in the world today, these ratios should be reflected in nature.

PGMs are mostly emitted in the metallic form, with a small soluble fraction. Palacios (2000) determined the soluble fraction of PGMs in exhaust fumes from autocatalysts. It was almost the same in fresh and aged (30000 km) catalysts; around 5 % of the total amount of PGMs emitted. Artelt (1999) found that platinum emitted from medium aged converters is to ≥ 99 % present in the metallic form. The platinum is bound to carrier particles. In new converters, >60 % of these particles have a diameter >10 μm and are thus not respirable. Only ~15 % have diameters ≤ 3 μm, thus capable of reaching the alveolar tract. The large particles (>10 μm) are most likely due to direct abrasion of the washcoat due to friction processes, while the small particles (<10 μm) mainly consist of aluminium oxide (Al_2O_3) on which the PGMs are deposited. The fraction of small particles seems to increase with increasing age of the converter (Artelt *et al.*, 1999). König (1992) suggested that very small exhaust gas particles (< 5 nm in diameter) containing platinum may coagulate or react with carbon particles in the exhaust gas and form larger platinum containing particles (up to 1 μm).

7.2 PGMs in environmental compartments

Table 2 summarises the PGM concentrations in different environmental compartments as known until now.

Table 2. PGM concentrations in different environmental compartments.

Compartment	Concentration			Unit	Note	Reference
	Pt	Rh	Pd			
Earth's crust	0.4	0.06	0.4	ng/g		Wedepohl (1995)
Urban air particles	2.9-70.8	0.4 -5.8	1.7-12.1	pg/m^3	Mean	Lu (2000)
Urban road dust	189-416	56-136	74-104	ng/g	<63 μm	Rauch *et al.* (1999a)
	164-388	56-100	140	ng/g	63-250 μm	
Roadside soil	25.3-253	4.8-39.7	1.2-12.5	ng/g	Topsoil, road distance 0.1 m	Cubelic *et al.* (1997)
Runoff water	15	-	-	ng/l	Median	Laschka *et al.* (1993)
River water	0.22-0.64	-	-	ng/g		Laschka and Nachtwey (1993)
Urban river sediment	4.8-15	2.5	-	ng/g		Rauch *et al.* (1999a)
Roadside grass	10.6	1.54	-	ng/g	Mean	Helmers and Mergel (1998)
Human serum	0.9	-	50.2	ng/l	Mean	Bergerow *et al.* (1997)
Human urine	1.02	11.7	9.5	ng/l	Median	Krachler *et al.* (1998)

7.2.1 Background levels

The Earth's crust contains around 0.4 ng/g of PGMs. Background levels in air samples are below 0.05 pg/m^3, in road sediments and soil in the pg/g range and in grass below 0.03 ng/g (Rauch and Morrison,

1999). Ocean sediments contain between 0.7 and 22 ng platinum/g (Hodge *et al.*, 1986). The geogenic background level of platinum, palladium and rhodium is 0.9, <0.5 and <0.7 ng/g, respectively (Zereini *et al.*, 1999).

Platinum group metals in the urban environment are found at levels considerably higher than the background concentrations in the Earth's crust and other environmental compartments as mentioned above, see table 2.

7.2.2 Airborne particles

Only a few studies have been performed on platinum in airborne particles. In a German study from 1989, platinum concentrations in air measured up to 13 pg/m^3. In the countryside, the concentrations were at maximum 1.8 pg/m^3. These levels could be considered as background levels, since the majority of all cars in Germany did not have catalytic converters at that time (Lindell, 1997).

Alt (1993) determined platinum content, particle size distribution and soluble platinum in airborne particulate matter. The total platinum content in the particles varied between 0.6 to 130 μg/kg and the total platinum concentrations in air was 0.02 to 5.1 pg/m^3, which increased up to 30 pg/m^3 near roads. The lowest platinum content was observed for the larger particles (> 8 μm). The amount of soluble platinum in airborne particulate matter was determined to be 30 to 43 % of the total amount of platinum.

Airborne platinum concentrations in Munich city buses was determined to range from 3.0 pg/m^3 on a suburban bus route to 33.0 pg/m^3 on the route with the highest traffic (Schierl and Fruhmann, 1996).

A recent study showed platinum, palladium and rhodium levels in air in the pg/m^3 range. A large number of samples were collected, and it was suggested that PGMs are not distributed homogeneously in air particles. Most particles contained low amounts of PGMs (around 2 pg/m^3) while a few particles had very high levels of PGMs (around 100 pg/m^3). Therefore, previous studies which only included a small number of data might be erroneous, due to the high variance among samples. It was found that the ratio between platinum and rhodium in airborne particles was around 4.2, approximately the same as in catalytic converters (around 5). For high PGM concentrations, however, the Pt/Rh ratio was around 11. The suggested explanation for this was that these particles originate from a converter consisting of Pt only, used in diesel vehicles. The Pt/Rh ratio in such catalysts is quite high. It could also be that the particles originate from aged three-way catalysts. A study showed that the Pt/Rh ratio in aged catalysts changes to around 12. Therefore, it was suggested that the air particles originate from traffic (Lu, 2000).

7.2.3 Soil and road dust

Total concentrations of platinum and rhodium in road sediments have increased since 1984 and particularly since 1991 (Rauch *et al*., 1999a). It is proven that traffic is the source of PGMs, in part since there is a sharp concentration trend depending on the distance from the road (figure 13). Almost all of the PGMs are deposited within the first 2-5 metres of distance from the roadway.

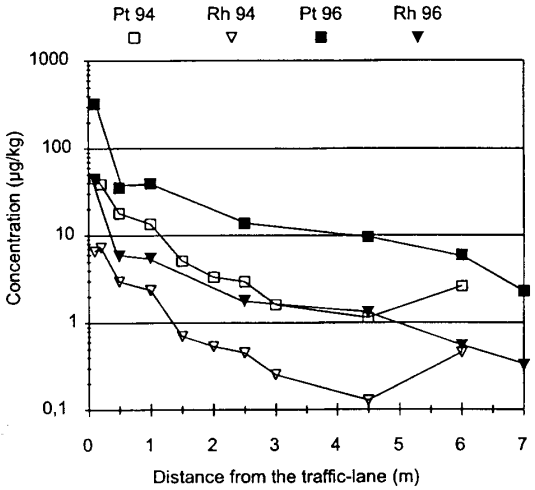


Figure 13. Pt and Rh concentrations in the upper soil (0-2 cm) versus distance from traffic lane at a German highway (Schäfer et al., 1999).

Swedish studies show that platinum concentrations in road sediment (in the smallest fraction studied: < 63 μm) increased as much as from 3.0 ng/g in 1984 to 8.9 ng/g in 1991 and to 28 ng/g in 1999 (Wei and Morrison, 1994a and Rauch *et al.*, 1999a). In the same studies, rhodium concentrations increased from 1.4 ng/g in 1984 to 3 ng/g in 1994 and to 5 ng/g in 1999. It was also found that PGM concentrations in road dust are in most cases higher in the < 63 μm fraction of the dust particles. It was suggested that the occurrence of PGMs in the 63-250 μm fraction partly might be due to the agglomeration of small particles. It was found that platinum has a higher association to Si, Al and K than to Fe and Mn, which shows the affinity of platinum for the autocatalyst particles (containing aluminium). Platinum and palladium associate to cerium in road sediments, while rhodium does not. The association suggests that platinum and palladium remain bound to the autocatalyst particles and have a poor mobility (Rauch *et al*., 1999c). The platinum found in road sediment is largely in an inorganic form, and it has a significant exchangeable fraction. This may lead to the release of dissolved platinum during storm events. Platinum is attached to autocatalyst particles on the road surface (Wei and Morrison, 1994a).

Zereini (1997) found concentrations of platinum, palladium and rhodium in roadside soil of 61, 4 and 11 ng/g, respectively. These levels were significantly higher than the geogenic PGE background value in the study area of 0.9 ng/g. Other studies have shown platinum concentrations up to ~10 ng/g in soil near motorways, 310 ng/g in road dust and 1 μg/l in road runoff water (Laschka *et al*., 1996).

Analyses on the PGM content of roadside soil revealed concentrations of Pt, Pd and Rh that exceeded by far the natural geochemical background values, which are in the low ng/g range. Platinum deposited on roadside soil accumulates in the top layer. Platinum levels varied from several hundred ng/g in the upper 0-2 cm layer of the soil close to the road to background values at a distance of 20 metres from the road, compare to figure 13. Maximum Pd and Rh concentrations were 10 and 35 ng/g respectively. This shows that there is a very strong dependence on the distance from the highway. The PGM concentrations also decreased rapidly with depth. PGM concentrations in road dust and urban roadside soil are also directly correlated to traffic intensity, as shown in figure 14 (Schäfer and Puchelt, 1998).

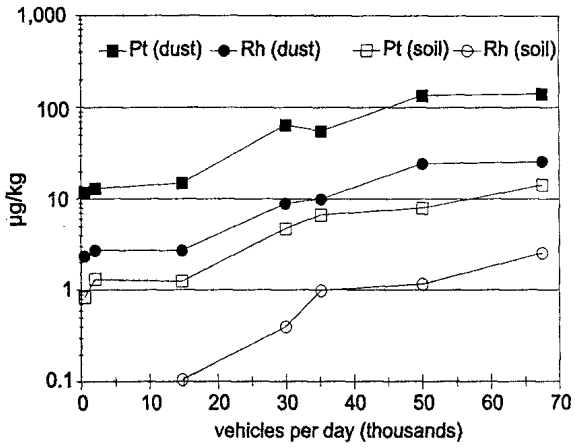


Figure 14. Platinum and rhodium concentrations in urban road dust and soil from Karlsruhe versus traffic intensity. (Schäfer and Puchelt, 1998)

7.2.4 Sediments

Rauch *et al.* (1999a) found Pt and Rh concentrations in urban river sediments of 4.8-15 and 2.5 ng/g. A recent study on platinum and palladium concentrations in sea sediments of the Boston Harbour, USA, showed that they had increased by 5 times background concentrations. The estimated background concentrations in this area was 0.2-0.8 ng Pt/g and 0.4-0.9 ng Pd/g, giving platinum and palladium concentrations of around 1-4 ng/g and 2-4.5 ng/g respectively (Tuit *et al*., 2000). Rauch *et al.* (2000) determined PGM concentrations in urban river sediments in Gothenburg, Sweden, using HR-ICP-MS. Pt, Pd and Rh levels were 1.0, 13.9 and 0.7 ng/g respectively. The Pd concentration is only indicative though, since Pd analysis was strongly interfered by several molecular ions that could not be separated by HR-ICP-MS.

7.2.5 Plants

Schäfer (1998) studied the uptake of platinum group metals by plants cultivated in a greenhouse on soil from a German highway. The concentrations in the plants reached up to 8.6 ng/g Pt, 1.9 ng/g Pd and 1 ng/g Rh. The bioavailability and uptake of PGMs by plants is described further in section 8.2.

Several studies show that there is an uptake of platinum into different organs of plants in the decreasing order: root > stem > leaf (Pallas and Jones, 1978; Ballach and Wittig, 1996). It has also

been found that the uptake of water is strongly disturbed by the high contents of platinum and other heavy elements in the nutrient solution (Ballach and Wittig, 1996).

Lustig *et al.* (1997) found that plants merely took up about 1 % of the platinum present in soil. It was also suggested that time is an important factor and that PGMs might be affected by long term processes. However, important factors such as the intensity of root penetration and the pot volume are not considered in this study, since the absolute amounts of PGMs in the pots instead of concentrations were compared with the plant uptake.

7.2.6 Animals

Rauch (1997) investigated biomethylation and levels of platinum in the freshwater isopod *Asellus Aquaticus* from a small river in Gothenburg, Sweden. Platinum levels ranged from 0.23 to 27.0 μg/g and it was found that platinum mostly was adsorbed on the exoskeleton of *Asellus Aquaticus.* A more recent study by the same author showed platinum, palladium and rhodium levels in *Asellus Aquaticus* of 1-100 ng/g, 75-300 ng/g and 1-50 ng/g, respectively. It was not investigated whether the PGMs were adsorbed on the exoskeleton or not.

Stevens (1998) has previously investigated platinum levels in Swedish raptors. The raptors investigated were sparrowhawks from rural and urban areas around Gothenburg, kestrels from southern Sweden, gyrfalcons from northern Sweden, captive peregrine falcons from the same breeding station as in this study and peregrines from northern and southern Sweden. Eggs, blood and faeces were analysed by cathodic stripping voltammetry (CSV). The results are presented in table 3.

Table 3. Platinum levels in egg, blood and faeces for different Swedish raptor populations. Adapted from Stevens (1998). (- = not analysed)

Bird	Egg (ng/g)	Blood (ng/g)	Faeces (ng/g)
PF, Captive	0.17	-	-
PF, N Sweden	0.102	0.15	0.44
PF, S Sweden	0.043	0.29	0.72
GF, N Sweden	-	-	0.17
Kestrel, S Sweden	0.14	-	-
SH City, S Sweden	0.51	-	-

The standard deviation is high; from 67 to 200 %, even though the sample size is relatively high (around 10). Seven out of ten values have a standard deviation higher than 100 %. This means that there is a large variation in PGM levels between different individuals of birds, even in the same group. Therefore, it is difficult to draw conclusions on the results.

A statistical test called the Mann-Whitney U-test was performed on the data in order to investigate if there are significant differences in Pt levels between different groups of raptors and biological materials. Significant differences in Pt concentrations in eggs were found between captive peregrines and southern wild peregrines, between wild northern peregrines and sparrowhawks and between wild southern peregrines and sparrowhawks. The most significant differences in Pt levels were found between eggs and blood and between eggs and faeces from sparrowhawks. There was also a significant difference in Pt levels between faeces from southern peregrines and gyrfalcons.

The platinum levels were higher in the blood than in the eggs, and even higher in the faeces. This is the opposite of the behaviour of most other toxins, for example mercury. The reason for the order of Pt concentration of faeces > blood > eggs is very difficult to explain, and depends on factors like absorption rate, solubility, speciation and low level accumulation, which are not yet completely understood for Pt.

The most unexpected result was that captive peregrines had significantly higher Pt levels than wild southern peregrines in their eggs. The captive peregrines are kept on a controlled diet of chickens bred up at the site. The only explanation was that a study by Vaughan and Florence (1992) showed that chickens contain high amounts of Pt compared to other foodstuffs.

The significantly higher platinum levels in the sparrowhawk from an urban area compared to wild peregrine falcons are suggested to be a result of different habitats. The platinum concentration increases with the proximity to urban areas, and sparrowhawks live closer to urbanisation than the wild peregrines.

There was a significantly higher Pt level in the blood than in the eggs of southern peregrines. It was expected to be the other way around. The suggested reason for the result was that prey species in the breeding areas (south-western Sweden) contain a higher amount of Pt than prey species in the wintering grounds (western Europe).

Significantly higher levels of Pt was found in the blood than in the faeces of southern peregrines. It was suggested that this might be due to that platinum is quickly absorbed by the body as it moves through the digestive system.

The suggested reason for the significantly higher Pt levels in faeces of peregrines in southern Sweden compared to gyrfalcons was that peregrines live in a more Pt-exposed habitat and that they migrate to western Europe during winter, where they are exposed to higher Pt levels than in Sweden, while gyrfalcons do not migrate at all.

It was also found that eggs from captive peregrines laid in the same clutch had low variation in Pt concentration. That means the females were not exposed to high Pt levels. Moreover, there would have been much more Pt in the first eggs than in the following if Pt had been bioaccumulating in the female. This did not happen, which means that it is doubtful that Pt is bioaccumulating. However, no conclusions could be drawn on whether Pt is bioaccumulating or not (Stevens, 1998).

7.2.7 Humans and human food

An Australian study showed high levels of platinum in meat (~3.2 ng/g), cereal products (~3.2 ng/g) and eggs (~3.5 ng/g). The concentrations were highest in liver, ca. 8 ng/g. Low levels were found in dairy products and vegetables. According to this study, the daily uptake of platinum for an adult person is ca. 1.4 μg/day (Vaughan and Florence, 1992). However, the reliability of this study is somewhat uncertain (Lindell, 1997).

Mean platinum concentrations of 160 ng/g wet weight in human fat, liver, kidney and pancreas have been reported (Vandiver *et al.*, 1976). Platinum concentrations in human blood and urine range between 0.8-6.9 ng/l and 0.5-15 ng/l respectively (Messerschmidt *et al.*, 1992). Several studies suggest that the correct background level of platinum in human blood is around a few ng/l (Lindell, 1997). In a more recent study by Krachler (1998), platinum, palladium and rhodium concentrations in human urine was determined to 1.0, 9.5 and 11.7 ng/l respectively.

7.3 Trends for the future

Helmers and Kümmerer (1999) calculated future platinum emissions and platinum concentrations in the environment. Based on traffic statistic data, emission rates (0.065 to 0.65 μg/km) and the share of cars with catalytic converters, figure 15 was outlined. 97 % of the cars are expected to have catalytic converters in Germany the year 2001. Figure 15 clearly shows how

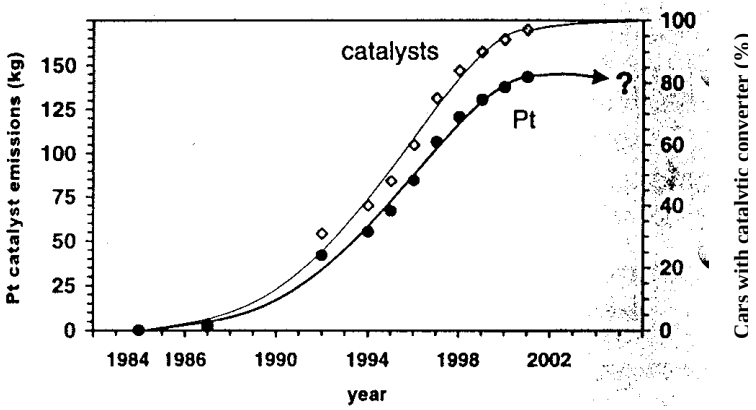


Figure 15. Platinum emissions per year from catalytic converters and share of cars equipped with catalytic converters in Germany extrapolated up to year 2001 (Helmers and Kümmerer, 1999).

platinum emissions from catalytic converters have increased over the past 25 years, directly correlating to the amount of catalysts. The trend for the future, however, seems to be decreasing platinum concentrations, due to the replacement of platinum by palladium since the beginning of the 90's. But this may be counteracted by the fact that ageing of catalytic converters will increase platinum emissions, leading to an overall increase of platinum emissions.

The extent of the platinum increase in the environment can be realised by comparing the pollution situations of lead (Pb) and platinum (figure 16). Pb levels are three orders of magnitude higher than Pt. That is due to the higher geogenic background level of Pb and to the higher level of Pb emissions. However, figure 16 shows that the magnitudinal increase of platinum in polluted soil and dust is 1000 times higher than the background level, while for Pb it is 10-100 times higher. This is alarming considering that platinum has only been emitted in relevant quantities for ten years, while lead has been emitted in high amounts for over 40 years (Helmers and Kümmerer, 1999).

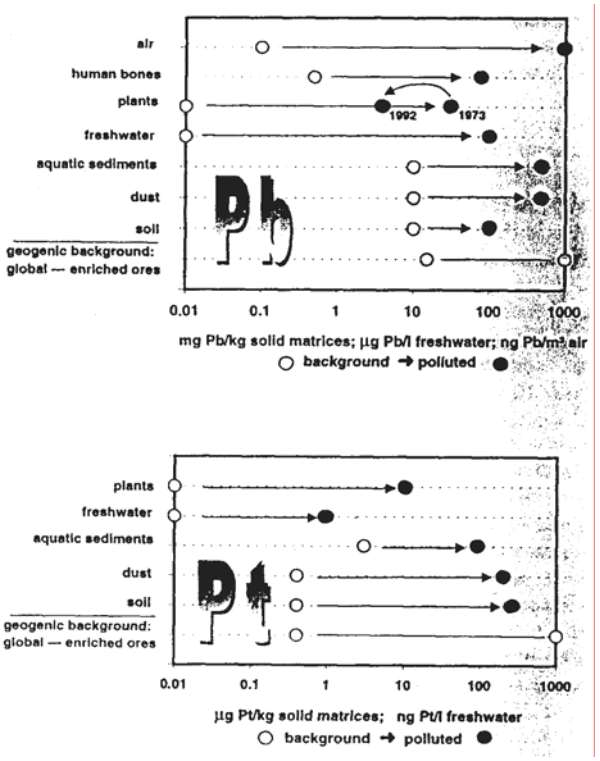


Figure 16. Pollution situations of Pb and Pt: comparison. Highly polluted matrices sampled immediately near a highway, mostly in south-western Germany. (Helmers and Kümmerer, 1999)

The study by Helmers and Kümmerer (1999) showed that Pt levels in soil and water predicted for the future were in the order of the geogenic background level (140 ng/kg) or lower. However, in the light of the comparison of the pollution history with lead (figure 16), the elevated platinum levels in the environment are alarming.

8. Effects of PGMs

8.1 Toxicology

Toxic effects of platinum in humans are illustrated in figure 17. Exposure to platinum occurs from exhaust catalysts, medication and different types of workplaces. The main target organs for toxicity are the skin, mucous membranes, the lungs and the kidneys. Indicators of platinum load are urine and hair (equal to feathers in birds). Platinum accumulates in the kidneys and the liver (Habashi, 1997).

Platinum in the form of cisplatin (cis-$[PtCl_2(NH_3)_2]$) is widely used in medicine as an anti-tumour drug. It inhibits DNA-synthesis. Cisplatin is strongly mutagenic and very toxic to bacteria (Lindell, 1997). Other side effects in humans are nausea and neurotoxicity (Rauch *et al*., 1999c).

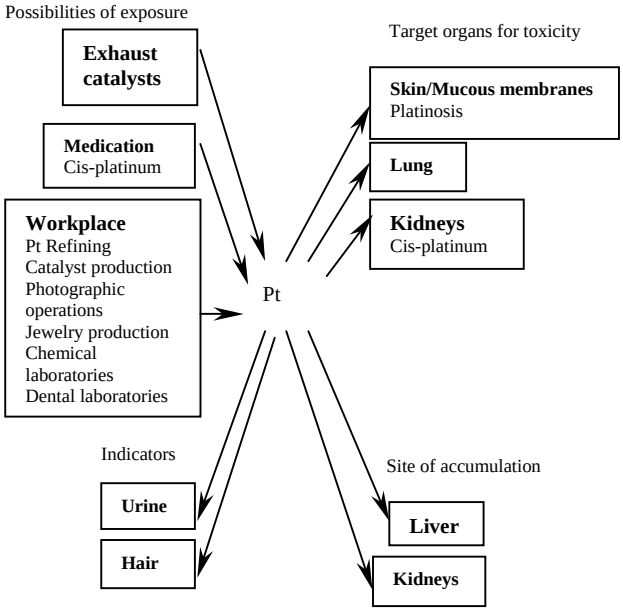


Figure 17. Toxic effects of platinum. (Habashi, 1997)

Water-soluble platinum compounds are in most cases more toxic than insoluble compounds (see Table 1). The metallic form of platinum seems to have a low acute toxicity when taken up orally, but very fine powder of the metal can be partially absorbed by the gastrointestinal tract, even though it is insoluble (Lindell, 1997).

Well-known effects of platinum compounds include strong allergy reactions, mainly due to the platinum salts. Platinum salts can cause contraction of the bronchi, anaphylactic chock and elevated levels of histamine in the plasma of animals at the first contact. Skin irritation is also a common effect of platinum salt exposure (Lindell, 1997).

In humans, it is generally considered that reactions caused by platinum salts in the airways and on the skin are of immunologic origin, but the exact sensitisation mechanism is still unclear. Symptoms begin after a sensitisation period, and merely a small part of the individuals exposed become sensitised. In addition, the affected individuals gradually become more and more sensitive to platinum and react at much lower levels than normal (Lindell, 1997). Sensitisation levels of 0.1 $\mu g/m^3$ have been reported for soluble platinum compounds (Artelt *et al.*, 1999). A 24-hour maximum exposure limit of 2 $\mu g/m^3$ of airborne, water-soluble platinum salts has been recommended by the U.S. Occupational Safety & Health Administration (Barefoot, 1997).

A study of workers in a platinum refinery industry showed that the chloroplatinates $(PtCl_6)^{2-}$ and $(PtCl_4)^{2-}$ are very allergenic. Neutral complexes and complexes that contained more strongly bound ligands were immunologically inactive, probably due to little or no contact with proteins (Lindell, 1997).

Platinum salts are toxic: the EC_{50} of platinum chloride for *photobacterium phosphoreum* is 25 μg/l (Wei and Morrison, 1994a). That is much lower than for example for copper (200 μg/l). The LC_{50} of Pt for *Asellus Aquaticus* is around 100 μg/l (Rauch, 1997). Lindell (1997) lists LD_{50}-values of different platinum compounds for rats and the value ranges from around 400 μg/g for the soluble compounds to around 2000 μg/g for the insoluble compounds.

Less is known about the toxicology of palladium and rhodium. However, it has been shown that palladium and rhodium are less cytotoxic and mutagenic than platinum (Bünger *et al*., 1996). A study by Wahlberg and Boman (1992) on the chemical relationship between palladium and nickel shows that palladium possesses a relatively high allergenic potential when it is in an ionic form. A concern is that palladium is generally found in higher concentrations than platinum in environmental materials, which indicates a higher bioavailability and mobility of palladium.

8.2 Bioavailability and pathways in the environment

Bioavailable compounds can more easily be taken up by organisms and bioaccumulate in tissues. In general, there are two mechanisms for the transformation of platinum group metals into bioavailable species:

1. Biochemical transformation (biomethylation into bioavailable species) via micro-organisms, such as bacteria (Lustig *et al*., 1997a).
2. Chemical oxidation, where the metal reacts with oxygen and forms complexes with ligands present in the soil. It has been shown that up to 3 % of the total metal is dissolved within 21 days by platinophile complexing agents in an oxygen atmosphere (Freiesleben *et al*., 1993).

One of the ways metals can become bioavailable to organisms is through biomethylation. Methylation is a chemical reaction where a methyl group is introduced to a compound instead of a nitrogen ion. Reactions between methylcobalamin (MeB_{12}), the methylated form of vitamin $B_{12,}$ and metal or metalloid ions have been used as a model system for the biomethylation of toxic elements. Methylation of platinum requires platinum in both oxidation states, Pt(II) and Pt(IV). These platinum compounds can be methylated by methylcobalamin. However, this has only been observed in laboratories and it is not possible to say if micro-organisms in the natural environment can biomethylate platinum compounds. In general, the methylated organometallic derivatives are more toxic than their inorganic precursors to higher organisms, due to the possible increase in lipid solubility, volatility and persistence in biological systems resulting from the methylation (Fanchiang, 1979; Ridley *et al.*, 1977). However, a German study investigated the influence of micro-organisms on the dissolution of metallic platinum emitted by autocatalysts. It was found that micro-organisms do not

influence the transformation of platinum compounds into bioavailable species in short term processes. There was no difference in results between soil in sterile and non-sterile conditions, indicating that transformation of platinum in soil is mainly of chemical nature (Lustig *et al.*, 1997a). On the contrary, a study by Wei and Morrison (1994b), suggested that platinum in urban gullypots occurring in an organic form is a result of bacterial action. However, in the light of the study by Lustig (1997a) that can also be explained by chemical dissolution in the presence of organic ligands such as humic acids. According to a study by IPCS (International Programme on Chemical Safety) it is not possible to draw any conclusions whether micro-organisms in the environment can biomethylate platinum compounds or not (Lindell, 1997).

The other way of metals to become bioavailable to organisms is through chemical oxidation in soil. Platinum species formed by chemical oxidation are predominantly attached to the soil, but they can be remobilised to a few percent with water and even more effectively with platinophile complexing agents like EDTA (Ethylene Diamine Tetra Acid) (Lustig *et al.*, 1996). Metallic platinum (Pt(0)), especially when ultrafine dispersed and in the nanocrystalline form, can be easily dissolved by natural complexing agents in organic matrices, resulting in possibly bioavailable platinum species. Metallic platinum is first oxidised with oxygen and then a potent complexing agent removes the platinum oxide formed as soluble complexes. However, without the presence of a complexing agent, the surface of Pt(0) is rapidly saturated with the oxide, inhibiting further oxidation. It was found that the naturally occurring ligand that has the greatest effect on the dissolution of metallic platinum is L-Methioneine (L-Met). On the other hand, ligands like humic acids in soil immobilise the dissolved platinum to sparsely soluble species, unless a stronger complexing agent is present (such as EDTA). The amount of dissolved platinum mainly depends on the particle size (Lustig *et al.*, 1998).

Even if the dissolved platinum species are relatively insoluble and immobile in soil, they may become bioavailable for plants, since plants have complexones that are similar to EDTA. Platinum in plants binds to high molecular weight proteins under natural conditions, i.e. when taken up by all parts of the plants (Lustig *et al.*, 1996). Lustig (1997b) found that the bioavailability of catalyst emitted platinum to plants was remarkably low. The platinum species were oxidised and immobilised in the soil. However, it was suggested that long-term processes might remobilize the absorbed platinum species and make them available to plants. Schäfer (1998) found a measurable transfer of PGMs from contaminated soils to plants. Pt, Pd and Rh transfer coefficients were in the range of immobile to moderately mobile elements, the same as Cu. The transfer coefficient is defined as the ratio of the concentration in the plant and the concentration of the element in the soil (c_{plant}/c_{soil}). The transfer coefficient in all plants decreased from Pd > Pt ≥ Rh, palladium therefore being the most biologically available of the PGMs. Palladium had a biological availability similar to Cu and Zn, sometimes also like Cd. Brooks (1992) found much higher concentrations of palladium than platinum in plants

growing on PGM ore deposits, which correlates to the finding of Schäfer (1998) that palladium is the most biologically available PGM metal.

Zereini (1998) found that lake sediments had significantly higher Pt/Pd ratios, indicating a higher geochemical mobility of palladium than platinum. Palladium in sediment is more readily transported out of the sediment to other environmental compartments than platinum, i.e. more mobile in the environment.

There are also examples of platinum bioaccumulation in animals. For example, bioaccumulation of platinum and palladium has been reported to be abnormally high in species of the bacteria *Pseudomonas* (Peterson and Minski, 1985). Platinum is also taken up and accumulated in the freshwater isopod *Asellus Aquaticus.* Two mechanisms have been suggested for this platinum uptake: binding to metallothionein-type proteins and accumulation in intracellular granules. Granules can explain the accumulation of high levels of metals without any apparent toxic effect. In addition, granules can associate with the exoskeleton and may be excreted each time the exoskeleton is lost, providing an efficient depuration mechanism. Platinum accumulation is species dependent. In *Asellus Aquaticus*, Pt(IV) is accumulated to a higher extent than Pt(II). LA studies indicated that palladium and rhodium have a different mobility from platinum and due to this, rhodium seems to exhibit a greater accumulation in *Asellus Aquaticus* in urban rivers. However, it could not be concluded whether platinum is biomethylated or not (Rauch *et al*., 1999c). Stevens (1998) found some indications on Pt not bioaccumulating in raptors. That was in part due to significantly higher levels of platinum in blood than in eggs, which is the opposite of what it should be if Pt was bioaccumulating. Low variations of platinum in different eggs, and a lower Pt level in the first egg than in the second egg laid in the same clutch of one female also suggests that Pt is not bioaccumulating. That is because the female would have sequestered as much Pt as possible into the first egg if Pt was bioaccumulating. However, there was no evidence strong enough to either support or reject the theory of Pt bioaccumulating in raptors.

In a study by Artelt (1999), platinum bioavailability was calculated by totalling the platinum content in urine and all organs except the lung in rats. Within 24 h the fastest clearance processes such as expiration and ciliary clearance were completed. The bioavailable platinum was mainly found in the urine, the relative contribution of urine to the bioavailable fraction of platinum increased steadily with time, reaching ≥ 87 % after 90 days. In contrast to urine, bioavailable platinum in blood decreased substantially with increasing time and reached very low levels after 90 days (≤ 0.03 %). The remaining platinum was mainly found in the kidneys and the liver. Using a model substance which closely resembles catalyst-emitted platinum, it was concluded that a substantial fraction (20-30 %) of the platinum originally present as metallic platinum in the form of ultrafine particles in the nanometer range was bioavailable after inhalation. In body tissues and fluids, ≥ 90 % of the bioavailable platinum

was bound to proteins, the rest was in the form of ionic complexes. It was suggested that the bioavailability of platinum is due to its unexpected in vivo solubility (10.0 %), which most likely is due to its ultrafine structure (Artelt *et al*., 1999). Another study investigated the whole body retention of platinum compounds after inhalation in rats, and it was found that it was species dependent: $PtCl_4$ > $Pt(SO_4)_2$ > PtO_2 > Pt (Moore *et al.*, 1975).

Studies on human tissue have shown that only Pt(II) binds to proteins in human blood, but Pt(IV) can be reduced to Pt(II) before binding. Platinum is transported with proteins to the liver and kidneys, where it accumulates before being excreted. In the liver and kidneys, platinum binds to metallothioneins (MTs). MTs are low molecular weight proteins which contain a lot of cystein. As long as metals bind to MTs they are considered harmless. The association constant of Pt(II) to MTs is approximately 30 and 107 times higher than that of cadmium and zinc, respectively. Thus, binding of Pt(II) to MTs can be caused by the replacement of zinc or cadmium atoms bound to MTs (Rauch *et al.*, 1999b).

Figure 18 is a model for the pathways of platinum group metals in the environment, based on the present knowledge about PGM behaviour. It is adapted to the scope this study and shows the possible route of PGMs from the autocatalyst to the raptors, considering that the main uptake of PGMs occurs through the diet. The PGMs might have been transformed on the way from the catalyst to the raptors.

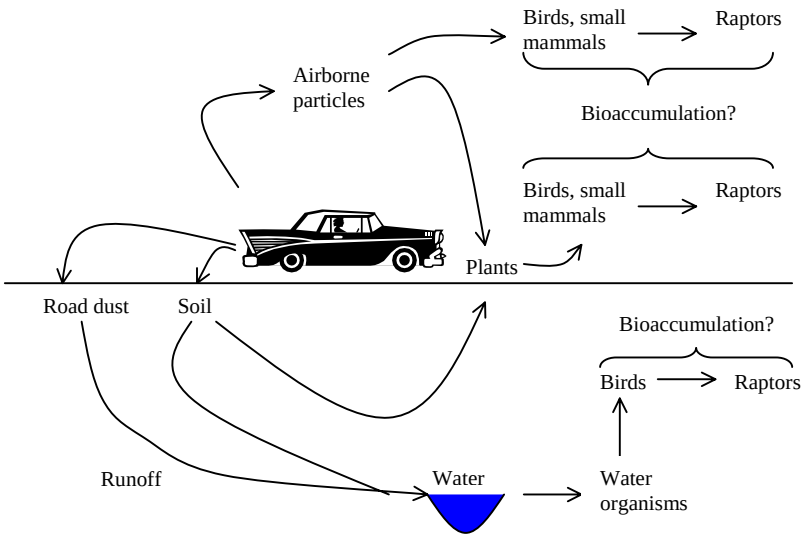


Figure 18. Possible route of PGMs from autocatalyst to raptors.

9. Inductively Coupled Plasma - Mass Spectrometry

Inductively coupled plasma-mass spectrometry (ICP-MS) was developed in the USA, and the first commercial instrument for ICP-MS was introduced in 1983 (Houk, 1985). Since then, the technique has developed rapidly and it is now a well-established and powerful analytical technique for the determination of trace and ultra-trace elements in a number of biological samples (Krachler *et al.*, 1998).

The ICP is used as the ion source and the MS is used to detect the ions produced by the ICP. The ICP operates at atmospheric pressure, while the MS requires a pressure of 10^{-5} torr. Therefore, a crucial component of the ICP-MS is the interface between these pressure regions. The ICP-MS used in this study is a Perkin Elmer Elan 6000. Samples can be introduced to the ICP by several techniques. The techniques used in this study, pneumatic nebuliser and laser ablation, are described in chapters 9.3.1 and 9.3.2. In short, the sample is introduced to a high temperature plasma (5000 K), commonly argon, which dissociates molecules and ionises atoms. Thereafter, the ions are passed into vacuum via a sample and skimmer cone interface, where the ion beam is focused into a quadrupole mass spectrometer. Here, the ions are sorted by the mass-to-charge ratio and detected by a scanning electron multiplier (American Geophysical Union, 1995). This is described more in detail below. However, at a given time, only ions of one given m/z (mass/charge) ratio have a stable path through the mass analyser to the detector. This means that signals from different elements cannot be measured at the same time. Instead, the ICP-MS is a sequential multielement measurement in which very little time is lost switching from one element to the next (Houk, 1985).

After being introduced by some kind of a sample introduction technique as described in chapter 9.3, the sample enters the ICP. First, the sample is introduced to the ICP torch, an assembly of quartz tubes (figure 19). The plasma is generated inside and at the open end of the torch. The sample is introduced to the plasma through the centre tube. The temperature in the induction region of the

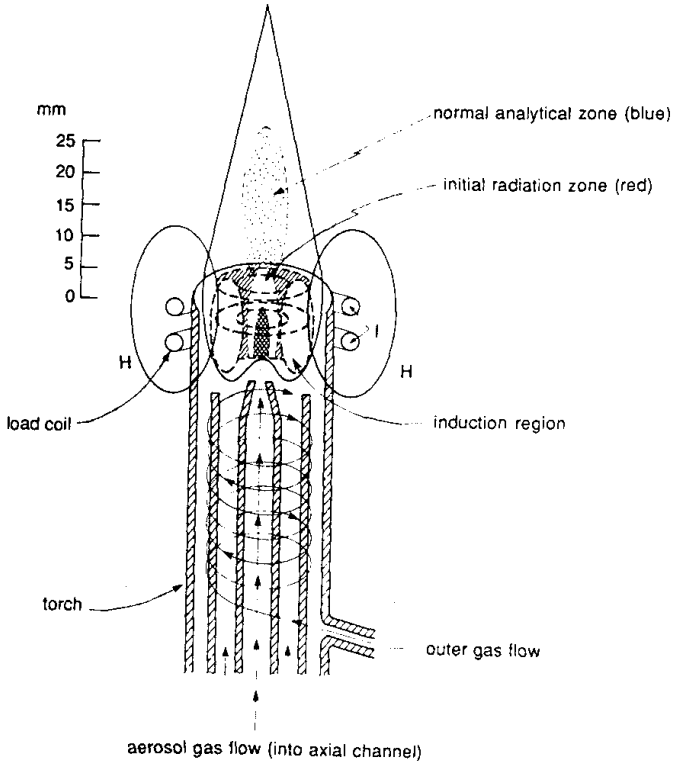


Figure 19. The ICP torch, gas flows and the induced magnetic field (Jarvis et al., 1992).

plasma may be as high as 10000 K. In the normal analytical zone, the temperature is around 5000 K. The outer gas flow, called the coolant flow, protects the tube walls and it is the main plasma support gas. The coupling or load coil consists of 2-4 turns of fine copper tube and it is cooled by a water or gas flow. It is located a few millimetres below the mouth of the torch (Jarvis *et al*., 1992).

The pathway for an analyte species through the ICP, the sampling interface and the mass analyser is depicted in figure 20. The analyte species spends approximately 2 ms in the hot plasma (E) where it is efficiently atomised and ionised. The plasma is maintained by RF (radio frequency) energy, which is transmitted to the plasma through the load coil (A). The plasma flows around the tip of a water-cooled metal cone called the sampler (F). In the tip of the sampler cone there is a circular orifice (opening) with a diameter of 0.5-1.0 mm. The sample is introduced into the axial channel (C), goes through the plasma (E) and then enters the orifice. Most of the gas flow is evacuated by a mechanical pump that maintains the pressure in the sampling cone on 1 torr (= 1 mm Hg = 1/760 atm = 133.32 Pa). The central orifice of the skimmer cone (G), also around 1 mm in diameter, is located behind the sampler at such a position that as much of the sampled beam (I) as possible is transmitted into the high vacuum chamber. In the high vacuum chamber, on the other hand, the pressure is only 10^{-4}-10^{-5} torr. The interface between these different pressure regions is the most crucial part of the ICP-MS. The ions reach supersonic velocities as they expand into the high vacuum chamber and they reach the skimmer orifice in only a few microseconds. The low pressure in the high vacuum chamber and the long mean free path allows for the ion lenses (K) to collect, focus and transmit the ions to the quadrupole mass analyser (M). The ion lenses provide only little or no m/z separation of the ions. Instead, that is done by the quadrupole mass analyser. The ions to be separated are introduced along the axis into one end of the quadrupole structure at velocities determined by their energy and mass. A given RF voltage will give only ions of one given m/z-value a stable path through the mass analyser. All other ions will be deflected too much. The ions of the selected m/z value are detected in an electron multiplier (N), the most common detector used in ICP-MS. In order to be observed by the MS, the ion must be present in the ICP and survive the extraction process or be formed by chemical reactions during the extraction process (Houk, 1985; Jarvis *et al*., 1992).

The sampling orifice in the ICP used in this study is made of nickel. Nickel has a good thermal conductivity, stability and machinability, and it does not interfere with PGM ions (Houk, 1985).

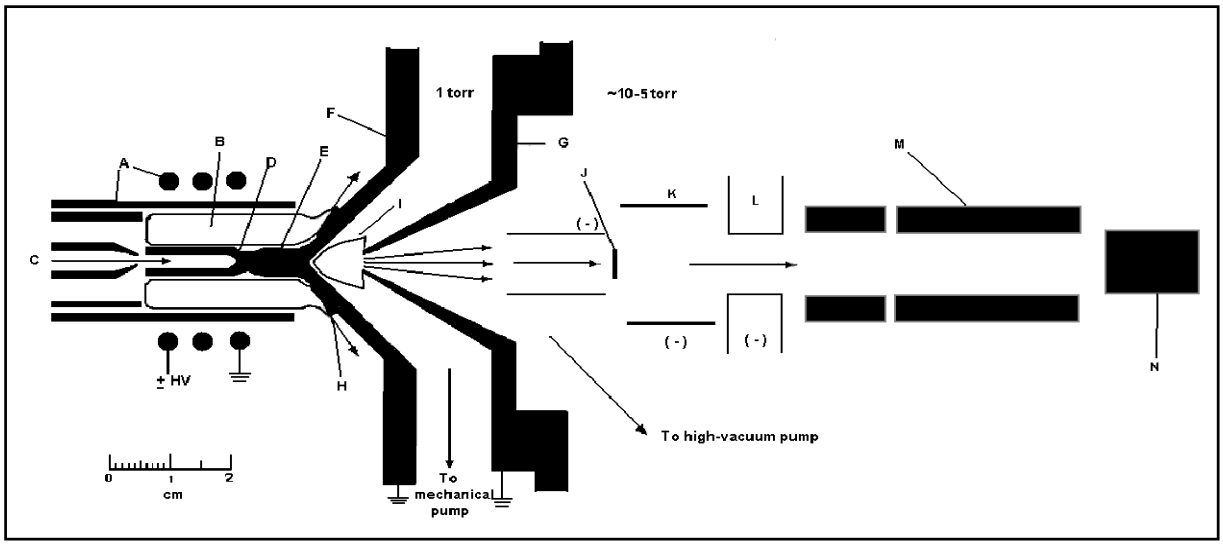


Figure 20. ICP, sampling interface and mass analyzer for ICP-MS (Jarvis et al., 1992).

(A) torch and load coil (HV = high voltage), (B) induction region of ICP, (C) solution aerosol being injected into axial channel, (D) initial radiation zone, (E) normal analytical zone, (F) nickel cone with sampling orifice in tip, (G) skimmer cone, (H) boundary layer of ICP gas deflected outside sampling orifice, (I) expanding jet of gas sampled from ICP, (J) shadow stop, (K) single ion lens, (L) differential aperture, (M) quadrupole mass analyzer, and (N) detector.

The advantages of the ICP-MS technique are that it can perform direct analysis of solutions and calibration against aqueous standards, that the detection limits for many elements are in the pg/l range, that is has a wide elemental coverage and a linear dynamic range up to 10 orders of magnitude (Durrant, 1999). The detection limit for liquid samples in the ICP-MS is 0.6 ng/l for platinum, 3.3 ng/l for palladium and 0.9 ng/l for Rh (Gomez *et al*., 2000).

Analytical difficulties of ICP-MS include spectroscopic and non-spectroscopic interferences, which are discussed more in detail in the next paragraph. Motivated partly by these difficulties, alternative sampling methods started to be used with ICP-MS, such as laser ablation (LA), described more in detail in chapter 9.3.2. LA offers reduced sample preparation, a rapid sample exchange and throughput, reduced spectroscopic interferences and the possibility of in situ spatially resolved analysis (Durrant, 1999).

9.1 Interferences

Analysis by ICP-MS suffers from two kinds of interferences; spectral (spectroscopic) and non-spectral (non-spectroscopic) interferences or matrix-effects.

A non-spectral interference is characterised by a reduction or increase in the analyte signal due to factors influencing the sample transport, ionisation in the plasma, ion extraction, or ion throughput in

the resulting ion beam. The nature and concentration of the sample matrix also influences the behaviour of this kind of interference (Evans and Giglio, 1993). Non-spectral interferences can be avoided by using an appropriate internal standard and spectral interferences can be avoided by using a sufficiently high spectral resolution or to estimate the contribution of the interference and correct mathematically or by applying matrix separation (Parent *et al.*, 1997).

Spectral interferences are caused by atomic or molecular ions that have the same nominal mass (the same m/z ratio) as the ion that is being analysed. Therefore, those ions interfere with the analysis by causing an incorrectly large signal at the m/z ratio of interest. Spectral interferences can be further divided into two types: interferences caused by overlapping isotopes of different elements, and molecular ion and doubly charged ion interferences (figure 21) caused by polyatomic ions formed from precursors in the plasma gas, atmospheric gases, water, acids used for dissolution and in the sample matrix. The polyatomic ions formed will interfere on analytes with the same m/z value. The most likely sources of polyatomic ions are from: 1) condensation reactions in the expansion region, 2) collisional reactions in the boundary layer around the outside surface of the sampler and 3) survival through the plasma (Evans and Giglio, 1993).

The potential spectral interferences for the Pt, Pd and Rh isotopes of interest in this study are listed in Table 4.

Table 4. Potential spectral interferences on Pt, Pd and Rh. Adapted from Krachler et al., 1998.

Analyte	Possible interference	Abundance of interferent (%)	Minimum resolution (m/Δm)
^{195}Pt	$^{179}Hf^{16}O$	13.6	8200
	$^{177}Hf^{18}O$	0.04	8800
	$^{178}Hf^{17}O$	0.01	6900
^{105}Pd	$^{89}Y^{16}O$	99.76	27 600
	$^{36}Ar^{69}Ga$	0.20	92 000
	$^{87}Rb^{18}O$	0.056	28 400
	$^{88}Sr^{17}O$	0.03	1 000 000
	$^{87}Sr^{18}O$	0.014	30 900
	$^{40}Ar^{65}Cu$	0.003	7300
^{103}Rh	$^{40}Ar^{63}Cu$	68.89	8040
	$^{87}Rb^{16}O$	27.76	147 000
	$^{206}Pb^{2+}$	24.14	1248
	$^{87}Sr^{16}O$	6.99	102 900
	$^{85}Rb^{18}O$	0.14	17 200
	$^{38}Ar^{65}Cu$	0.02	7200
	$^{36}Ar^{67}Zn$	0.01	10 100

Minimum resolution is the resolution required to separate the interferent and analyte masses in the ICP-MS. The ICP-MS used in this study is a quadrupole ICP-MS, which cannot separate interferences by mass/charge ratio. The maximum resolution power today is 10000, which can be done by double focusing ICP-MS. This means that most interferences cannot be separated by the instrument.

Therefore, interferences will yield concentrations higher than the real concentrations of the analytes of interest, and this needs to be corrected for.

There are different ways of correcting for interferences on platinum group metals. Parent (1997) investigated correction methods for the hafnium oxide interference on platinum in the analysis of cordierite. This was done by comparing two mathematical correction methods; via the HfO^+/Hf^+ ratio (used in this study, see eq.1) and via standard addition of Hf, and a method for the chemical separation of Hf based on adsorption chromatography and isotope dilution. It was found that chemical separation was much more precise than the mathematical correction methods. Although results are less precise for Hf/Pt ratios up to 50, mathematical correction also yields accurate results. The best mathematical correction method for correction of HfO^+ interference was the standard addition of Hf.

Krachler (1998) investigated the influence of interferences on ^{106}Pd, ^{195}Pt and ^{103}Rh in the analysis of urine. It was found that effects of ^{106}Cd and $^{40}Ar^{66}Zn$ on ^{106}Pd and of $^{206}Pb^{2+}$, $^{87}Sr^{16}O^{40}$ and $Ar^{63}Cu$ on ^{103}Rh can not be disregarded. The doubly charged ion $^{206}Pb^{2+}$ could contribute with up to 50 % of the whole signal of ^{103}Rh, and the polyatomic ions $^{87}Sr^{16}O^{40}$ and $Ar^{63}Cu$ could contribute up to 15 % of the total ^{103}Rh signal. Contribution from the interferences $^{40}Ar^{66}Zn$ and ^{106}Cd to the total ^{106}Pd signal was up to ca. 50 %. All other interferences on ^{106}Pd were neglected because of scarce abundance, extremely low concentrations in urine or because no appreciable influence on the total signal could be found. HfO+ interference on ^{195}Pt was also neglected because of low concentration in urine.

The main interferences for all of the platinum isotopes are the hafnium oxides (HfO^+). The isotope ^{195}Pt, which has been analysed in this study, is mainly interfered by $^{179}Hf^{16}O$. In this study, the hafnium oxide interference was corrected mathematically via the HfO^+/Hf^+ ratio using equation (1):

$I_{Pt} = I_{Pt,s} - (I_{Hf,s} R_{HfO})$ (1), where

I_{Pt} = the corrected Pt signal,

$I_{Pt,s}$ = the Pt signal measured for the sample solution,

$I_{Hf,s}$ = the signal for Hf in the sample solution and

R_{HfO} = the previously determined HfO^+/Hf signal ratio. (Parent *et al*., 1997)

The amount of HfO^+ that forms in the argon plasma is strongly dependent on the temperature of the plasma and, if the sample has been nebulised, on the size of the drops (Lustig *et al*., 1997). Other ways of optimising the reduction of oxides based on CeO/Ce are to adjust the nebuliser gas and RF power and trying to stabilise the temperature of the plasma.

The major interfering species on ^{105}Pd are YO^{+}, ArCu, SrO and RbO. On ^{106}Pd, the main interfering species are ZrO, ArZn and Cd. The most common way of calculating the palladium concentration is to calculate the signal of the ^{105}Pd isotope. Thus, the corrected ^{105}Pd signal is the measured signal subtracted by the signal of the interfering species (Y, Cu, Sr and Rb) multiplied by the signal ratio of each interference (eq.(2)).

$$I_{Pd} = I_{Pd,s} - (I_{Cu,s}*R_{Cu,Pd} + I_{Y,s}*R_{Y,Pd} + I_{Sr,s}*R_{Sr,Pd} + I_{Rb,s}*R_{Rb,Pd}) \quad (2)$$

The major interfering species on ^{103}Rh are Pb^{2+}, CuAr, SrO and RbO. An example of spectral interference on ^{103}Rh is shown in figure 21. The signal of rhodium is corrected according to the same principle as platinum and palladium, i.e. the measured rhodium signal for the sample solution is subtracted by the signal of the interfering species (Cu, Sr, Rb and Pb) multiplied by the signal ratio of each interference (eq.(3)).

$$I_{Rh} = I_{Rh,s} - (I_{Cu,s}*R_{Cu,Rh} + I_{Pb,s}*R_{Pb,Rh} + I_{Sr,s}*R_{Sr,Rh} + I_{Rb,s}*R_{Rb,Rh}) \quad (3)$$

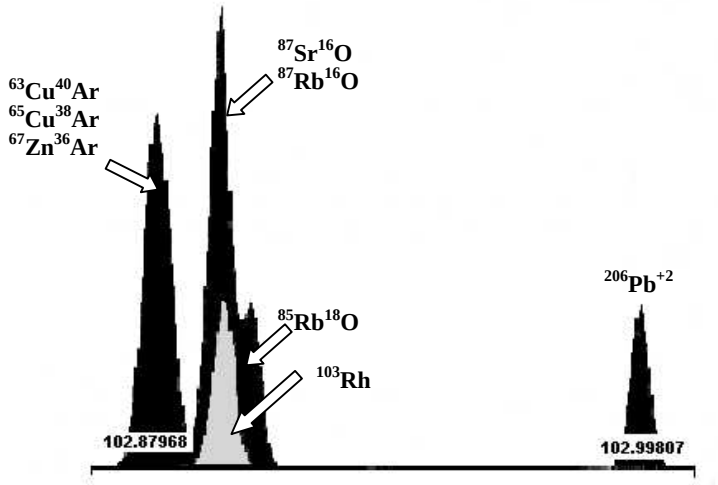


Figure 21. Spectral overlapping on ^{103}Rh in HR-ICP-MS analysis (Lustig et al., 1999).

9.2 Sample preparation

9.2.1 Microwave digestion

Microwave digestion techniques have become popular in the last decade, mainly because they are less time consuming, more reproducible and more accurate than conventional digestion techniques (Krachler *et al.*, 1998). However, microwave procedures can more easily lead to contamination of the samples, since analytes previously absorbed on the walls of the digestion vessels might be released into the samples. Therefore, it is of great importance to clean the vessels thoroughly with acid before and after use.

The microwave digestion system used in this study is called CEM MARS 5. The principle of microwave digestion ICP-MS is illustrated in figure 22.

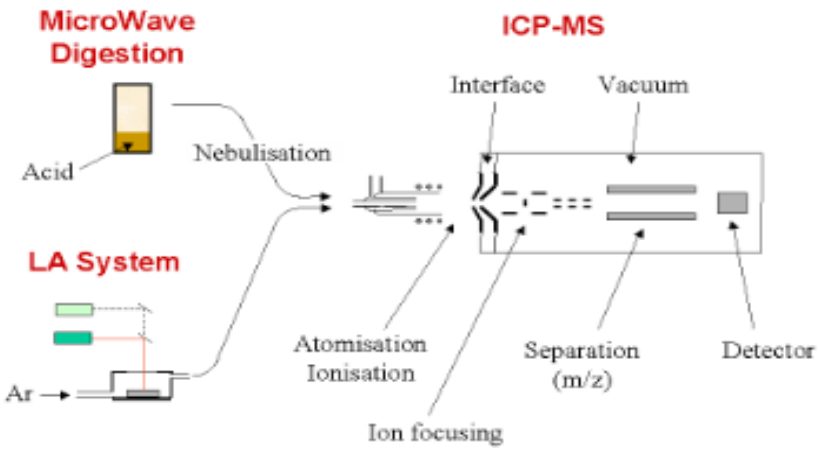


Figure 22. Illustration of the ICP-MS technique with different sample introduction techniques.

When digesting feathers using a microwave, the feathers are first dissolved in aqua regia in closed digestion vessels. The dissolving process is speeded up by heating the samples with microwave radiation. Using closed digestion vessels makes it possible to reach higher temperatures because the pressure that is generated within the vessel raises the boiling point of the reagents (Jarvis *et al*., 1992).

After cooling down, the samples of dissolved feathers are completely evaporated and then redissolved in HCl in order to remove the aqua regia and to adjust the volume. After this procedure, the samples can be analysed in the ICP-MS. The samples are introduced to the ICP via a pneumatic nebuliser (figure 22). The nebuliser is described more in detail in chapter 9.3.1.

9.3 Sample introduction techniques

9.3.1 Pneumatic nebuliser

The pneumatic nebuliser is used to introduce liquid samples to the ICP (figure 22). Samples are introduced to the nebuliser by a peristaltic pump. In the nebuliser, a high velocity gas stream (commonly argon) produces a fine droplet dispersion of the analyte solution. Droplets with a diameter larger than around 8 μm are removed by a spray chamber. The smaller droplets only make up about 1 % of the solution. These droplets are injected to the plasma torch ((C) in figure 20). This technique is

considered very inefficient, but it is also convenient, reasonably stable and it is easy to use with multiple sample changers (Jarvis *et al.*, 1992).

9.3.2 Laser ablation

Laser stands for 'light amplification by stimulated emission of radiation'. An illustration of the technical principle of a LA-ICP-MS is presented in figure 23. An ultraviolet (266 nm, frequency quadrupled) pulsing laser beam is focused onto the sample cell. The sample sits within a quartz ablation cell and the sample surface can be viewed via a camera. The sample remains at atmospheric pressure. A computer-controlled turntable allows positioning of the sample in the x, y and z-directions (Durrant, 1999). The laser ablates particles from a solid material and the particles are swept into the ICP by argon gas via a teflon tube. Since air must not enter the ICP, an arrangement for cell purging to atmosphere is also included.

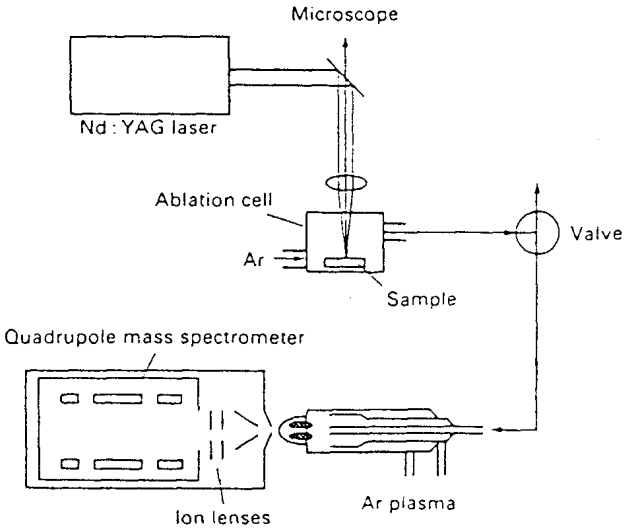


Figure 23. Schematic diagram of a typical LA-ICP-MS system (Durrant, 1999).

The laser used in this study is a Nd:YAG laser and it operates in Q-switched mode. Nd:YAG means 'neodymium-yttrium aluminium garnet', and it consists of $Y_3Al_5O_{12}$. The laser wavelength output from the Nd:YAG is 1064 nm and this beam is quadrupled to the wavelength 266 nm. Q-switched means that practically all laser energy is contained in a short laser pulse of approximately 10 ns. The sample is ablated by subjecting it to laser pulses. A Q-switched (Q mode) pulse is produced by rapidly changing the quality (Q) factor, which is a measure of the energy storage capacity of the laser (Durrant, 1999). In Q-switched mode, much of the ablation occurs through total vaporisation and mechanical ablation (American Geophysical Union, 1995). Argon gas is used to transport the ablated material and the plasma also consists of argon. Argon is used mainly because of its transparency and lack of emission lines in the wavelength region 200-400 nm (Houk, 1985).

The particle transport efficiency to the ICP is low for small particles (< 5 nm), since they tend to be lost by diffusion. Larger particles (> 3 μm) tend to settle due to gravity, which makes the transport efficiency for such particles low as well. Particles with a size between these extremes are carried to the ICP with an efficiency of > 80 %. The overall efficiency of the system is defined as the fraction of ablated material that is ionised in the ICP. This depends on the particle size distribution, the transport

function of the sample cell and the transfer tube, and on the response function of the ICP (Durrant, 1999).

One of the advantages of LA as a sample introduction system is the greatly reduced oxide interference. Decreases in intensity of up to 2 orders of magnitude for a number of O-, N-, H- and Ar-containing species has been observed (Evans and Giglio, 1999). The oxides are reduced so much that they can be neglected, but there are still some Ar-, N- and H-containing species which cannot be neglected. A dry sample, which is introduced to the plasma, does not give polyatomic interference species produced by the interaction of water and acid species with the argon plasma. In addition, laser ablation allows for the direct analysis of solid samples, which means that no potentially contaminating dissolution processes are needed. Other advantages compared to comparable techniques are that it can analyse both conducting and non-conducting material without a conductive coat and/or other charge balancing techniques and that no vacuum is required in the sample chamber (American Geophysical Union, 1995). The main difficulty in LA-ICP-MS is to obtain fully quantitative analyses (Durrant, 1999).

The most important laser parameters are the wavelength, mode (Fixed-Q or Q-switched), focusing, laser energy and number of shots. Lower wavelengths give better spatial resolution, lower fractionation effects and improved analytical precision. The lowest wavelength used today is 193 nm, which is used in the excimer laser. Optimum sensitivity is often obtained when focusing below the sample surface. However, the laser used in this study is not focused. In most cases, greater laser energy, producing greater ablated material, also leads to a greater response in the ICP for a constant analyte concentration. However, excess ablated material can cause blocking of the sampling-cone orifice, memory effects and plasma disequilibrium. Particles that deposit in the sample cell or in the cell-ICP transfer line can be re-suspended in the cell flow in subsequent analyses and thus give memory effects. Blockage of the sampling-cone orifice leads to erratic responses and will eventually shut down the ICP. If too much material is ablated for the ICP to volatilise and ionise, the result will be plasma disequilibrium, which prevents quantification (Durrant, 1999).

The most important parameters in the analysis with laser include the number of elements to be analysed, the quadrupole settling time, the dwell time, the number of sweeps per reading, readings per replicate, number of replicates and points per spectral peak. The settling time is the time it takes for the detector response to stabilise after a peak hop in the selected m/z value. The dwell time is the integrating time per selected m/z value. The recommended relation between the dwell time and the settling time when using the laser is 6:1, because it will give the shortest time not used for measuring (~15 %) (Durrant, 1999).

Detection limits in LA-ICP-MS are closely related to the signal intensity, the counting time per element for the ablation mass and on the sample cell design. These factors will affect the size and configuration of the ablation crater, i.e. on the amount of material ablated. The precision of the LA-ICP-MS is dependent on fluctuations in the intensity signal. These fluctuations are due to variations in the amount ablated between different laser pulses. Therefore, the precision depends on the amount of material reaching the plasma (American Geophysical Union, 1995).

Elements can be quantitatively determined by normalising the intensities of the peaks to an internal standard. Internal standardisation removes the need of knowing an accurate volume of ablated material reaching the ICP torch (American Geophysical Union, 1995). However, it can be quite difficult to find an appropriate internal standard and you also need to be aware of elemental fractionation.

10. Method

The idea was to compare sparrowhawk to gyrfalcon, to compare urban to rural sparrowhawks, to compare peregrine falcons from northern Sweden to those from southern Sweden and to compare wild peregrine falcons to those captive. Comparisons of sparrowhawks and wild/captive peregrine falcons, northern peregrines and gyrfalcons and peregrine falcons from before 1986 and wild peregrine falcons were also to be made. In order to examine to what extent the prey contributes to the exposure of PGMs to raptors, levels of PGMs in the house-sparrow (main prey of the sparrowhawk) and the willow-grouse (main prey of the gyrfalcon) were examined. The PGM concentrations in the bird's body are reflected in the feathers, since feathers are in contact with the blood as they grow. Thus, feathers were analysed in order to estimate the level of body contamination and to investigate how long the metals stay in the bloodstream, i.e. to obtain an idea about the metabolism rate of the metals in the bird's body. Feathers are also relatively easy to sample and quick to analyse.

In one sparrowhawk (SH Tuve), feathers from four different parts of the body were analysed. The feathers come from the tail, the wing, the neck and the belly. This analysis was performed because it is interesting to see if there are differences in the PGM levels between feathers from different parts of a bird's body.

In addition, a feather from a captive peregrine falcon was cut in eleven pieces and the pieces were analysed separately by ICP-MS. This was done in order to examine whether there is a difference in the PGM levels in different parts of the feather or not. That is interesting for this study because different parts of feathers have been analysed with the ICP-MS and it has to be known whether the results should be corrected or not, depending on which part of the feather it came from. It is also interesting to compare the changes in concentrations obtained by microwave digestion ICP-MS in the feather to the

LA-ICP-MS results for the same feather. This can be done by first ablating the feather by laser and then cutting it into pieces, dissolving it and analysing it by ICP-MS.

10.1 Samples

Feathers from sparrowhawk, peregrine falcon, gyrfalcon, willow-grouse (called grouse further on in this study) and house-sparrow (called sparrow further on in this study) were analysed. All feathers used for the analysis are listed in Table 5 with information on the date and site the feathers were collected, sex and type of feather. Primaries are feathers from the wing. Date means date of collection.

Table 5. Feathers used in ICP-MS analysis (microwave digestion and/or laser ablation).

	Date	Site of collection	Sex	Type of feather
Sparrowhawk (SH)		Flåta, Norway (rural)	Male	
	1990	Vegårshei, Norway (rural)	Male	
	91-06-15	Änggården (urban)		Primary
	94-05-24	Strekered (rural)		Primary
	94-05-25	Biskopsgården (urban)		Primary
	96-05-24	Blixås (rural)		Primary
	96-06-03	Hökemossen (rural)		Primary
	96-06-15	Axelmossen (urban)		Primary
	96-06-15	Flagsjö V (rural)		Primary
	97-05-19	Duvekärr (rural)		Primary
	97-05-27	Kyrkobyn Dala (rural)		Primary
	97-07-21	Slottskogen (urban)	Female	Primary
	99-07-04	Tuve, Göteborg (rural)	Male	Primary, Tail, Belly, Neck
Peregrine Falcon (PF)	1976	Scotland	Female	
	1982	Falkenberg, Halland, S Sweden	Female	
	98-05-12	“OS”, Bohuslän, S Sweden	Female	Tail-feather
	98-05-15	“Hål”, Västergötland, S Sweden	Female	
	98-06	“DN”, Dalsland, S Sweden		
	98-07-08	“Helge”, Norrbotten, N Sweden		
	99-07	“Ronja”, Norrbotten, N Sweden	Juvenile female	
	1999	Captivity, S Sweden	Male	Tail-feather
	1999	Captivity, S Sweden	Female	Tail-feather
	99-12-22	Captivity, S Sweden, no. 42	Male	
	99-12-22	Captivity, S Sweden, no. 116	Female	
	99-12-22	Captivity, S Sweden, no. 64	Male	
	99-12-22	Captivity, S Sweden, no. 122	Female	
	99-12-22	Captivity, S Sweden, no. 388	Male	
	99-12-22	Captivity, S Sweden, no. 101	Female	
	99-12-22	Captivity, S Sweden, no. 120	Male	
	99-12-22	Captivity, S Sweden, no. 223	Female	
	99-12-22	Captivity, S Sweden, no. 349	Male	
	99-12-22	Captivity, S Sweden, no. 377	Female	
Gyrfalcon (GF)	99-06-14	“SE”, Norrbotten, N Sweden		
	99-06-14	“SF”, Norrbotten, N Sweden		
	99-06-15	“N10”, Norrbotten, N Sweden		
Grouse (G)	99-02	Västerbotten, N Sweden		
	99-04	Tarnadalen, Sarek, N Sweden		
Sparrow (S)	98-04-23	Axelmossen (urban)		
	98-05-18	Slottskogen (urban)		

10.2 Microwave digestion ICP-MS

Feathers analysed by ICP-MS after microwave digestion are listed in table 1, appendix 1. Table 6 shows the parameters used for the ICP-MS when analysing the samples.

Table 6. Settings for ICP-MS.

Instrument	**ELAN 6000**
Sample Introduction	
Sample uptake	1 ml min^{-1}
Nebuliser	Cross flow
Carrier gas	Argon, 0.86 l/min
Cones	Nickel
ICP	
RF power	1000 W
Plasma gas	Argon, 16 l/min
Auxiliary gas	Argon, 0.9 l/min

Acquisition	
Analytes scanned	^{103}Rh, ^{105}Pd, ^{106}Pd, ^{195}Pt
Data acquisition	Peak hopping
Mass Resolution	Quadrupole
Dwell time	100
Sweeps per reading	10
Peak width	6

All the feather pieces consisted of only the feather shaft, except for the pieces in tubes 12a and 14a that had the vane remaining on the shaft. This was done in order to check whether the vane contains larger amounts of PGMs than the shaft.

Samples 3d-13d were pieces of a feather from a captive peregrine falcon. Sample 3d corresponds to piece 1 on the feather, i.e. the part of the feather closest to the bird's body, whereas sample 13d is piece 11 of the feather, which is the tip of the feather, see figure 24. Unfortunately, piece 6 was lost.

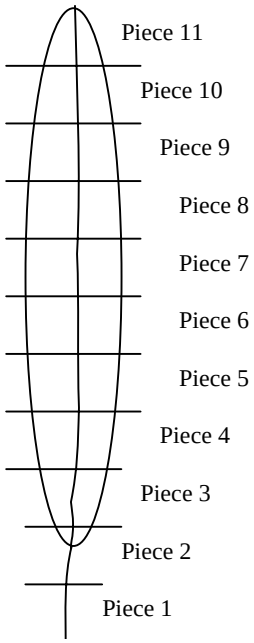


Figure 24. Division of the captive peregrine feather.

A feather piece was put in a digestion vessel and it was weighed (Appendix 1, Table 1). Then 6 ml of 30 % HCl (hydrochloric acid) and 2 ml of 65 % HNO_3 (nitric acid) (aqua regia) was added to the tubes.
The following reactions for platinum take place in aqua regia (Habashi, 1997):

$8\ HCl + 2\ HNO_3 + Pt \rightarrow H_2PtCl_6 + 4\ H_2O + 2\ NOCl$

$3\ HCl + HNO_3 \rightarrow Cl_2 + 2\ H_2O + NOCl$

The tubes were heated in the microwave oven for 30 minutes. The maximum temperature was 210°C and the pressure reached 150 psi. The tubes cooled down for approximately 1 hour until the temperature reached about 30°C. After that, the content of the tubes was poured into beakers. The liquid was evaporated using hot plates. The remains were redissolved in 5 ml of 2 % HCl. The liquid was poured into test-tubes and put in the freezer.

A few days later, the samples were analysed by ICP-MS. One representative isotope for each metal was analysed. ^{103}Rh is the only Rh isotope, ^{105}Pd was chosen because it has less interferences than ^{106}Pd and ^{195}Pt was chosen because it is the most abundant isotope and it is also less interfered than other Pt isotopes. In order to eliminate the influence of spectral interferences, standards of Hf, Sr, Rb, Cu, Pb and Y were analysed in the ICP-MS before the samples were analysed. The concentrations of the standards are listed in table 7.

Table 7. Concentrations of interference standards for ICP-MS analysis (ppb).

Interfering species	Standard 1	Standard 2	Standard 3	Standard 4
Hf	0.1	1	10	100
Sr	1	10	100	1000
Rb	1	10	100	1000
Cu	1	10	100	1000
Pb	1	10	100	1000
Y	0.1	1	10	100

Standards of Pt, Pd and Rh were also prepared and analysed before the samples for instrument calibration (table 8).

Table 8. Concentrations of PGM standards for ICP-MS analysis (ppb).

	Standard 1	Standard 2	Standard 3	Standard 4	Standard 5	Standard 6	Standard 7
Pt	0.01	0.05	0.1	0.5	1	10	50
Pd	0.01	0.05	0.1	0.5	1	10	50
Rh	0.01	0.05	0.1	0.5	1	10	50

In addition, an internal standard was added to samples 1b-14d, in order to correct for non-spectral interferences. The internal standard consisted of indium (In) (for Pd, Rh, Cu, Rb, Sr and Zn) and iridium (Ir) (for Pt, Hf and Pb) and the concentration was 10 ppb.

The interference standards (table 7) were used to calculate the ratio between the PGM intensity and the interference intensity, i.e. HfO+/Hf, ArCu/Cu, RbO/Rb etc. The corrected intensity signal was calculated according to eq.(1)-(3). In order to determine the concentration of Pt, Pd and Rh in the sample, the ratio between the measured intensity signal (apparent intensity) and the corrected intensity signal (real intensity) was multiplied by the apparent concentration of Pt, Pd or Rh. At this stage, the concentration is given in µg/l (c1), so in order to express it in ng/g (c2), the concentration was multiplied by the volume of the sample (5 ml) and divided by the weight of the feather (appendix), see eq.(4).

$$c2 = 1000*c1*V/m \qquad (4)$$

10.3 LA-ICP-MS

A piece of the feather shaft was cut off and placed in the glass ablation cell. The laser was adjusted so that the feather piece was in focus. A start and a stop point on the feather piece were chosen. Other factors to be set were the ablation type, laser energy level, spot size, scan speed, repetition rate of the laser pulse, dwell time, readings per replicate and sweeps per reading. Readings per replicate and sweeps per reading were chosen according to the length of the ablation line, therefore varying between different samples. The dwell time was 1-5 ms and the settling time around 1.5 ms. The most commonly used settings for the laser are listed in table 9.

Table 9. Settings for laser ablation.

Ablation type	Single line scan
Laser energy level	5-8 mJ
Scan speed	5, 10, 20, 50 µm/s
Spot size	5
Repetition rate of laser pulse	20 Hz

The laser ablated material from the feathers, which was swept to the ICP-MS by argon gas, and the ICP-MS analysed the material instantly.

11. Results and Discussion

11.1 Microwave digestion ICP-MS

11.1.1 PGM concentrations and sample sizes

Sample sizes, i.e. number of individuals and number of feathers, of the different groups of birds analysed by ICP-MS after microwave digestion are listed in table 10.

Table 10. Sample size of feathers analysed by microwave digestion ICP-MS.

	Number of individuals	Number of feathers
PF 1976	1	3
PF 1982	1	2
PF North	2	3
PF South	3	6
PF Captive	13	16
GF North	3	6
Grouse North	2	2
SH City (all)	1	1
SH City	5	9
SH Countryside	3	4
SH Norway	2	2
Sparrow City	1	1
Sparrow City (all)	1	1

Table 11 shows PGM concentrations, standard deviations and concentration range for all groups of birds. Mean concentrations of PGMs in shaft pieces of feathers from the different groups of birds examined, obtained by ICP-MS after microwave digestion, are shown in figure 25. PGM concentrations for each sample are shown in figure 1 in Appendix. PGM concentrations in the intact feathers of sparrowhawk and sparrow are shown in figure 26.

Table 11. Mean PGM concentrations, concentration interval and standard deviation (ng/g and %) in the birds studied. (n = number of samples/feathers)

		Pt				Pd				Rh			
	n	Mean (ng/g)	Range (ng/g)	Std Dev	%	Mean (ng/g)	Range (ng/g)	Std Dev	%	Mean (ng/g)	Range (ng/g)	Std Dev	%
PF 1976	3	0,20	0,07-1,13	0,181	90,8	0,40	0,24-0,55	0,219	55,0	0,23	0,14-0,27	0,078	33,6
PF 1982	2	1,70	0,53-2,87	1,651	97,1	4,04	2,55-5,54	2,110	52,2	1,38	0,19-2,57	1,688	122,4
PF North	3	1,21	0,17-2,37	1,105	91,2	2,35	1,24-2,94	0,961	40,9	3,10	0-9,09	5,189	167,4
PF South	6	1,63	0,06-3,70	1,176	72,2	5,29	1,09-10,82	3,082	58,3	2,62	0,54-5,11	1,691	64,6
PF Captive	16	1,38	0,09-4,33	1,367	99,2	2,35	0,04-10,08	3,226	137,2	0,96	0-7,51	1,184	123,4
GF North	6	1,28	0,55-2,50	0,243	19,0	1,33	0,57-3,41	0,625	47,0	0,34	1,11-0,58	0,335	16,2
Grouse North	2	0,55	0,18-0,93	0,534	96,5	0,65	0,31-0,98	0,489	75,0	0,34	0,24-0,45	0,144	41,7
SH City (all)	1	6,14	-	-	-	8,19	-	-	-	0,66	-	-	-
SH City	9	1,71	0-12,92	2,029	119,0	16,60	0,43-37,33	10,60	63,8	8,62	0-33,44	8,134	94,4
SH Countryside	4	1,05	0-2,16	0,282	26,8	9,28	6,20-29,49	9,156	98,6	3,79	0,97-8,48	3,118	82,2
SH Norway	2	1,79	1,27-2,32	0,745	41,5	0,48	0,32-0,65	0,235	48,8	1,38	1,18-1,38	0,038	2,7
Sparrow City	1	6,39	-	-	-	6,74	-	-	-	0,89	-	-	-
Sparrow City (all)	1	12,74	-	-	-	18,64	-	-	-	1,50	-	-	-

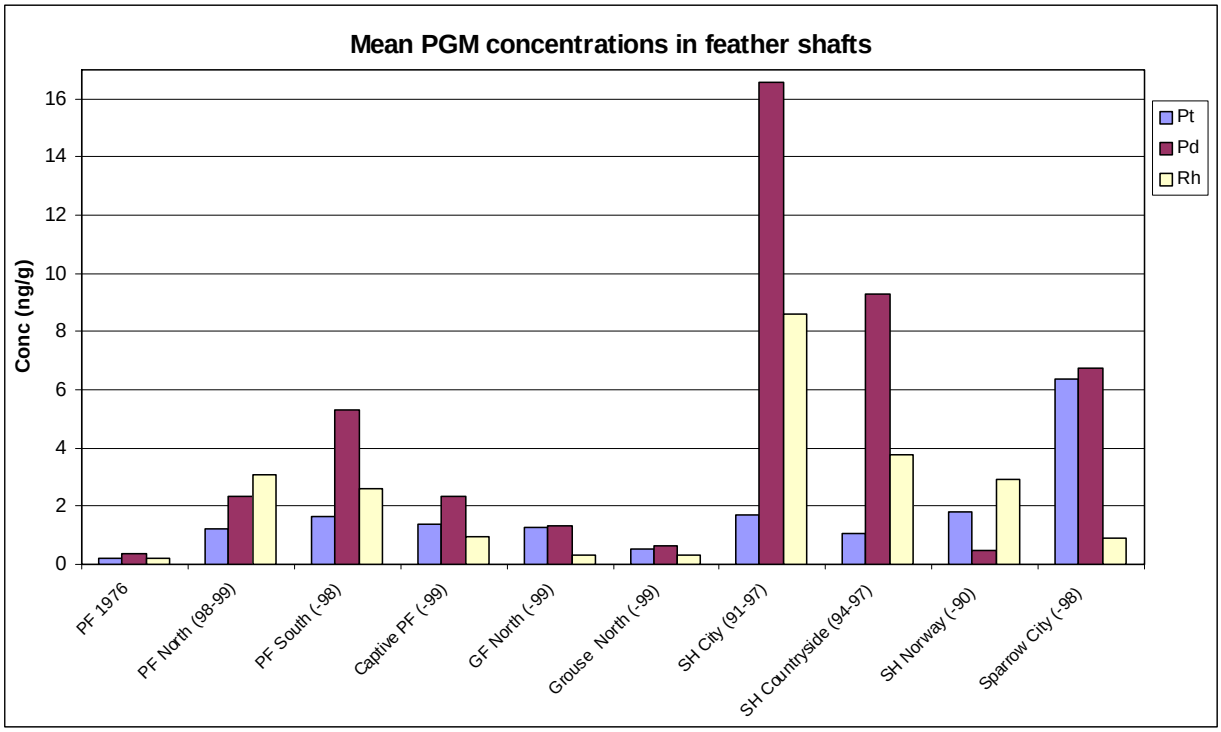


Figure 25. Mean concentration of platinum group metals in feathers of the birds studied. The years that the feathers were collected are also marked.

The mean total PGM concentrations in all feathers examined decrease in the following order: SH City > SH Countryside > Sparrow City > Wild PF > PF 1982 > SH Norway > Captive PF > GF > Grouse > PF 1976 (figure 25).

The mean concentration of platinum in the feather shafts varies between 0.2 and 6.4 ng/g, with the highest level in the sparrow-feather from the city. As expected, the lowest levels were found in the peregrine falcon from 1976 and in the grouse, because they are the least exposed birds. The mean concentration of palladium ranges from 0.4 to 16.6 ng/g. The highest levels of palladium were found in the sparrowhawks from the city and the countryside. The peregrine falcon from 1976, the sparrowhawks from Norway and the grouse had the lowest levels. Mean rhodium levels vary from around 0.2-0.3 ng/g in the peregrine falcon from 1976, the gyrfalcon and the grouse and up to 8.6 ng/g in the sparrowhawk from the city (Table 11).

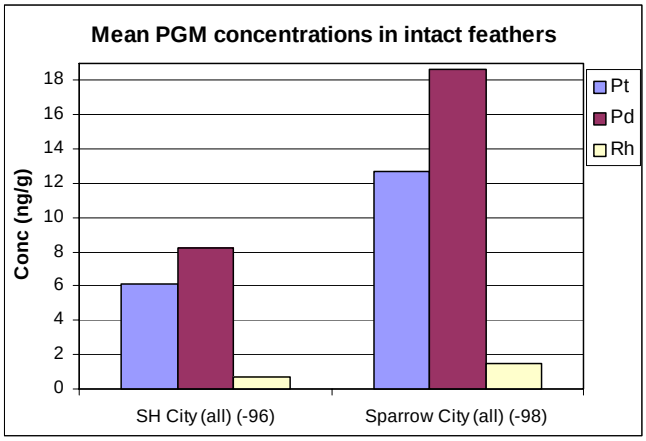


Figure 26. Mean concentration of platinum group metals in intact sparrowhawk and house-sparrow feathers.

The standard deviation is rather high for many samples; it is over 100 % for 5 concentration values (out of 30). The groups with large standard deviations are SH City, Captive PF, PF 1982 and PF North. Therefore, these mean values are rather uncertain. However, the large standard deviations and wide intervals could be explained by the fact that the groups consist of many different birds, especially SH City (5 individuals) and Captive PF (13 individuals) (table 11). Therefore, it can be difficult to obtain a consistent value, since there are large variations between different individuals. The other groups consist of 1-3 different individuals (Table 11). Other studies on metals (Al, Cd, Pb) in different bird species have shown that concentrations vary a lot, both within and between species (Solonen *et al.*, 1999). Stevens (1998) also found large differences in platinum levels within the same species of raptors; even with an average sample size of 9 individuals in each group, the mean standard deviation was around 126 %. So the high variance in PGM levels that was found in this study is probably natural, a common phenomenon in birds.

11.1.2 Mann Whitney U-test

Table 12 shows p-values that are calculated using the Mann-Whitney U-test. Groups of sparrowhawks, wild peregrine falcons and captive peregrine falcons were compared. This test determines if there is a significant difference in PGM concentrations between groups of birds. The p-value must be below 0.05 for the difference to be considered significant. The group of sparrowhawks consists of 10 individuals (5 from the city and 5 from the countryside). The wild peregrine falcons are both northern and southern peregrines, in total 5 individuals, and the group of captive peregrines consists of 13 individuals. As shown in table 12, the Mann-Whitney U-test showed that there were significant differences in the Pd and Rh concentrations between the feathers from sparrowhawks and captive peregrine falcons, but not for Pt. No significant differences were found between wild peregrine falcons and sparrowhawks and between wild peregrines and captive peregrine falcons. The main reasons for the high p-values are the small sample sizes and the large variance in PGM concentrations between the different individual birds. The sample sizes are too restricted to do a Mann-Whitney U-test for the other groups of birds. Preferentially, at least 10 individuals in each group are needed to do the test.

Table 12. P-values obtained by the Mann-Whitney U-test through comparison of sparrowhawks (rural + urban), captive peregrine falcons and wild peregrine falcons. The p-value must be below 0.05 for the difference to be considered significant.

	Pt	Pd	Rh
SH - Captive PF	0.256	0.0043	0.049
Wild PF - SH	1.0	0.1709	0.254
Wild PF - Captive PF	0.335	0.254	0.173

The only significant differences could be found in Rh ($p = 0.049$) and especially Pd ($p = 0.0043$) levels between urban and rural sparrowhawks and captive peregrine falcons, as shown in Table 12. The levels of platinum are on the same level, but palladium levels are around 7 times higher and the rhodium levels are almost 9 times higher in the sparrowhawks compared to the captive peregrine falcons. This supports the suggestion that Pt is on a constant level while Pd and Rh increase with increasing exposure. The concentration differences are most probably due to differences in habitat and food. Sparrowhawks live and hunt in urbanised areas while the peregrine falcons are held in captivity and the captive falcons are kept on a controlled diet, containing less PGMs than sparrows for example.

11.1.3 Bioavailability

Probably the most interesting result is that palladium levels generally are quite much higher than the levels of platinum. That is unexpected, since platinum is released from catalysts in equal or only slightly smaller quantities than palladium, according to the latest studies. This could show possible evidence that palladium is more mobile through the food chain than platinum. Furthermore, Pt is on a constant level, while Pd and Rh levels vary between different groups of birds. The Pt level is around

1.5 ng/g in all groups of birds except the sparrow, the peregrine from 1976 and the grouse. This suggests that Pt is not bioaccumulating, but rather remains on a background level independent of the level of exposure. On the contrary, Rh and especially Pd might be bioaccumulating, since levels are very different in different groups. Pd and Rh levels are for example much higher in more exposed birds (urban and rural sparrowhawks, sparrow) than in less exposed ones (gyrfalcons, peregrines). However, Pd and Rh levels in the raptors are not as high as they would be if they were bioaccumulating through biomethylation. So, this study suggests that Pd and Rh is not being biomethylated. However, this study does give indications on palladium and rhodium being more mobile in the environment and through the food chain than platinum. Another support for this statement was found when calculating mean Pt/Pd and Pt/Rh ratios for each of the different groups of raptors. The average Pt/Pd ratio decreased in the following order: GF > Wild PF > Captive PF > SH Countryside > SH City, from 0.9 to 0.06. The Pt/Rh ratio decreased in a similar order: GF > Captive PF > Wild PF > SH Countryside > SH City, from 5 to 0.125. These orders are similar to the order of increasing concentration in the feathers, as described previously. This indicates that rhodium and especially palladium increase in the blood of the raptors, i.e. bioaccumulate, while Pt does not. That would be the reason why the difference between Pt and Pd or Rh increases as the concentrations increase.

Gyrfalcons generally seem to have a bit higher PGM concentrations in their feathers than their main prey, the grouse, has. This could also mean that the metals are accumulating the further up you go in the food chain.

The house-sparrow living in the city has a higher Pt level, but less Pd and Rh, compared to urban sparrowhawks. This is most probably due to that the sparrow is granivorous, while the food choice of the sparrowhawk is small birds. This is another indication that at least Pd and Rh might be bioaccumulating, since the levels seem to be increasing the higher you go in the food chain (sparrows → sparrowhawks). The sparrow also contains large amounts of PGMs as previously assumed. Interesting is that when analysing only the feather shaft (‘Sparrow City’), the PGM levels are much lower than they are when analysing an intact feather, with both shaft and vane (‘Sparrow City (all)’) (figure 25 and 26). However, it must be kept in mind that only one intact feather and one feather shaft was analysed. The intact sparrow-feather contains more Pt and Pd than only the shaft of the sparrow-feather. This could mean that the dust-bathing makes dust particles containing PGMs attach to the vane of the feather, which results in high amounts of PGMs on the feathers. Sparrowhawks ingest a small amount of feathers from their prey while eating, so this is one possible pathway of PGMs into the raptors’ bodies. However, it is not known if the particles attached to the outside of the sparrow-feathers are bioavailable. It is more likely that PGMs inside the body of sparrows are more easily available to sparrowhawks.

11.1.4 Comparisons between groups of birds

Urban and rural sparrowhawks from Gothenburg also seem to have about the same levels of Pt, but more Pd and Rh than sparrowhawks from Norway. However, these results could not be verified with the Mann-Whitney test. The results seem logical though, since sparrowhawks from Norway live in areas even less urbanised than the sparrowhawks living in the Gothenburg countryside. The fact that the platinum level is higher and the palladium level so much lower in the sparrowhawks from Norway seems inconsistent and it might be due to the low sample size (n=2). Both urban and rural sparrowhawks also seem to have much higher levels of Pd and Rh than gyrfalcons, but almost the same level of Pt. That is most likely due to differences in habitat; gyrfalcons live in mountain areas of northern Sweden, which are less exposed to PGMs from for example car catalysts.

As expected, sparrowhawks in the city seem to have higher levels of PGMs compared to sparrowhawks from the countryside, although no significant difference was found with the Mann-Whitney test since the sample size was too small. However, many individuals in the rural areas shift their hunting grounds in the winter from the countryside to urbanised areas where there is more food at that time. Thereby, rural sparrowhawks may be exposed to higher PGM levels in winter.

It seems like PGM levels are generally a little bit higher in the northern peregrine falcons than in the gyrfalcons from the same region, although no significant difference could be established (Mann Whitney U-test). The Pt concentration is on the same level for both groups though, which supports the suggestion that Pt is on a constant level regardless of exposure. The higher Pd and Rh levels in peregrines might be explained by the fact that peregrines migrate to south-western Europe, where they are exposed to higher levels of PGMs than in northern Sweden, while gyrfalcons do not migrate at all. Another reason might be that peregrine falcons feed on aquatic bird species (in an aquatic food chain), while gyrfalcons feed on grouse, belonging to a terrestrial food chain. That is because aquatic organisms take up contaminants via the gills or the skin from the surrounding water. Metals may also bioaccumulate more readily in tissues of animals feeding on other aquatic animals, than they do in animals belonging to a terrestrial food chain. However, wild peregrine falcons from southern Sweden seem to have a little bit higher levels of Pt and Pd, but lower levels of Rh, than the wild peregrine falcons from northern Sweden. This contradicts the hypothesis that birds belonging to an aquatic food chain would have higher PGM levels than birds in a terrestrial food chain.

Wild peregrine falcons from southern Sweden seem to have about the same level of Pt but more Pd and Rh compared to captive peregrine falcons, which is due to higher PGM exposure. However, no significant difference was found (Mann Whitney U-test). The captive peregrine falcons have low

levels because they are kept on a controlled diet of captive chickens. Thus, they are not subjected to high PGM levels through their food. Wild southern peregrine falcons also have much higher levels of all PGMs than the peregrine falcon from 1976, but approximately the same levels as the peregrine falcon from 1982. The relatively high levels in the peregrine falcon from 1982 might be explained by the large standard deviation in this group. The values for the peregrine falcon from 1976 should be more reliable.

11.1.5 Increase since 1976

The background level is suggested to be around 0.2 ng Pt/g, 0.4 ng Pd/g and 0.2 ng Rh/g, since these are the lowest levels found in the raptors. These levels were found in the wild peregrine falcon from 1976, before autocatalysts were used, so it seems reasonable to believe that this could be a background level. Compared to these background concentrations, PGM levels have increased by approximately 10 times in wild peregrine falcons since 1976. Correspondingly, the levels have increased by approximately 4-40 times in the other raptors since 1976, with the largest increase in the urban sparrowhawk and the lowest in the gyrfalcon.

11.1.6 External/internal contamination

Comparing the PGM concentrations in an intact sparrowhawk-feather (‘SH Axelmossen (all)’) to the levels in the shaft of the same sparrowhawk-feather (‘SH Axelmossen’) reveals generally lower levels in the intact feather (figure 27). Pt levels are higher in the intact feather, while the Pd and Rh levels are much higher in only the shaft. Although only one intact feather was analysed, the results suggest that sparrowhawks are not exposed to PGMs that attach to the feathers superficially, i.e. from airborne particles, road dust etc. They are rather subjected to PGMs through ingestion of contaminated food, such as feathers from sparrows. Therefore, preening of their own feathers is suggested not to be an important route of PGM exposure to sparrowhawks.

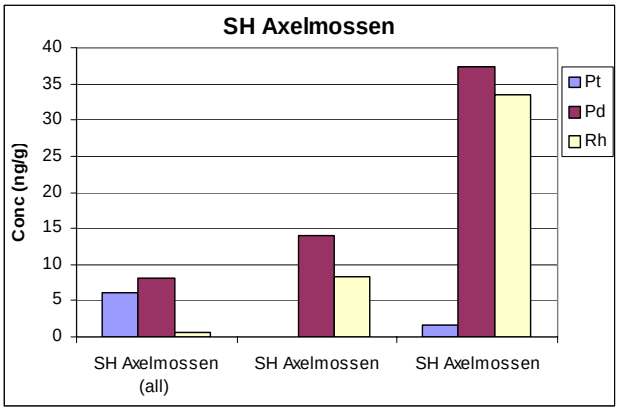


Figure 27. PGM levels in an intact feather compared to the shaft of a feather.

11.1.7 Variations between feather types

Figure 28 shows the PGM concentration in feathers from different parts of a sparrowhawk body. Feathers were taken from the tail, the wing (primary), the belly and the neck, in total four samples. The samples are too few to say anything conclusive about the distribution of PGMs in feathers from different body parts of a bird, but it seems like there is slightly more PGMs in the tail-feather as compared to the others. However, the levels are very low, making it difficult to see a clear difference between the samples. All other feathers analysed in this study are primaries or tail-feathers. Therefore, it should be kept in mind that tail-feathers might possibly show higher amounts of PGMs than the primaries even in the same bird when comparing PGM levels in different birds and different feather-types (see table 12), even though it very uncertain. Table 13 shows the concentrations of PGMs in the different feather-types, together with mean concentrations, concentration interval and standard deviation. The standard deviation is around 50 %. Mean PGM concentrations are much lower than in other sparrowhawks from areas around Gothenburg, both rural and urban.

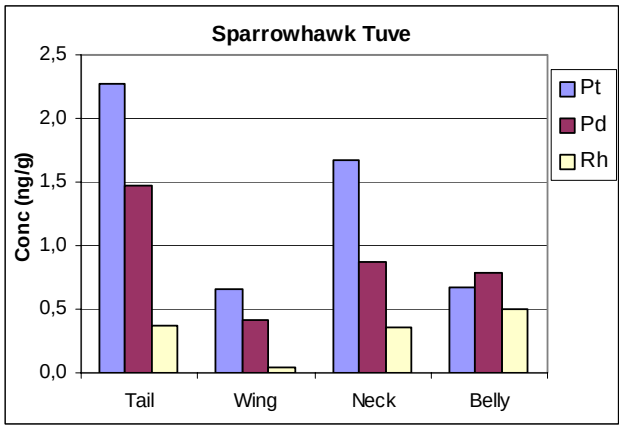


Figure 28. PGM concentrations in feathers from different body parts of a sparrowhawk from Tuve, Gothenburg.

Table 13. Mean PGM levels, interval and standard deviation for feathers from different body parts of a sparrowhawk from Tuve, Göteborg.

	Pt (ng/g)	Pd (ng/g)	Rh (ng/g)
Tail	2,28	1,47	0,37
Wing	0,65	0,42	0,05
Neck	1,67	0,87	0,35
Belly	0,67	0,78	0,50
Mean (ng/g)	*1,32*	*0,88*	*0,32*
Range (ng/g)	*0,65-2,28*	*0,42-1,47*	*0,05-0,5*
Standard deviation (ng/g)	*0,796*	*0,436*	*0,192*
Standard deviation (%)	*60,3*	*49,2*	*60,4*

11.1.8 Variations between different feather parts

It was also investigated whether PGM concentrations vary along the shaft of a feather or not by cutting a captive peregrine feather in pieces as described in chapter 10.2. Figure 29 shows the PGM concentrations that were found along the shaft of the feather. Piece 11 was discarded because of difficulties in weighing the small piece. There seems to be no large differences in PGM concentrations in different parts of the feather. It is possible that concentrations might increase a little bit closer to the

tip of the feather (figure 29). One must remember, however, that this is only one analysis, so no statistical calculations can be made. The levels can be elevated in parts of the feather if the bird has experienced high PGM concentrations in the blood for a longer time period, which is reflected in the feather. But generally, it is likely that PGM concentrations do not vary significantly along feathers, although more feathers should be analysed this way to establish such a theory. Table 14 shows the PGM concentrations in the different pieces and mean levels, interval and standard deviation of Pt, Pd and Rh. The standard deviation is rather high for all elements, especially Pd and Rh. Mean concentrations are in the same range as the other captive peregrine falcons analysed in this study (table 11).

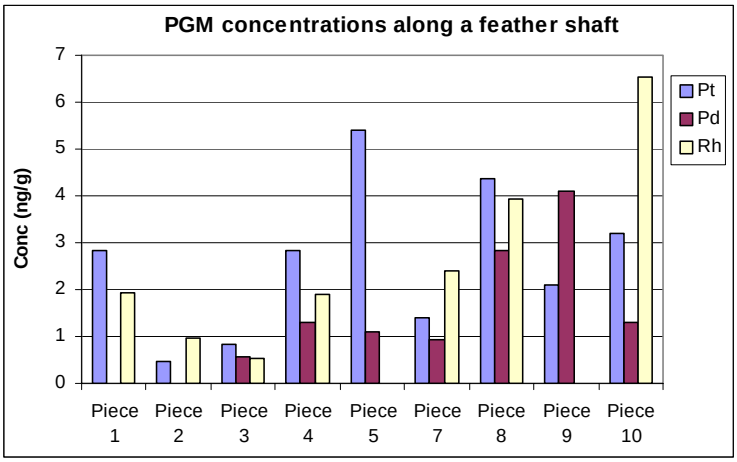


Figure 29. PGM concentrations along the feather shaft from a captive peregrine falcon.

Table 14. Mean PGM levels, interval and standard deviation for different parts of a feather from a captive peregrine falcon.

	Pt (ng/g)	Pd (ng/g)	Rh (ng/g)
Piece 1	2,82	0,00	1,93
Piece 2	0,46	0,00	0,97
Piece 3	0,82	0,57	0,53
Piece 4	2,85	1,31	1,90
Piece 5	5,39	1,09	0,00
Piece 7	1,41	0,92	2,40
Piece 8	4,37	2,84	3,93
Piece 9	2,10	4,10	0,00
Piece 10	3,21	1,29	6,54
Mean (ng/g)	*2,61*	*1,35*	*2,02*
Range (ng/g)	*0,46-5,39*	*0-4,10*	*0-6,54*
Standard deviation (ng/g)	*1,614*	*1,337*	*2,115*
Standard deviation (%)	*61,9*	*99,3*	*104,5*

11.1.9 Differences between sexes

A weak tendency of higher Pt and Pd levels in males compared to females was also observed in the captive peregrines, but no significant differences could be found (Pt: $p = 0.175$, Pd: $p = 0.426$). Higher levels in males than in females might suggest that females have additional ways of excreting Pt and Pd from their bodies than do males. This could be done through sequestering into eggs, which has been shown to occur for mercury in herring gulls (see chapter 5.1). This should be further investigated also in wild raptor populations, where differences might be clearer.

11.1.10 Comparison to another raptor study

It is a bit difficult to compare the results in this study to the results from the previous study by Stevens (1998) on platinum in raptors, since this study only focuses on concentrations in feathers, while the former did not obtain any results for feathers. However, the results from this study show higher levels of platinum than found in that study. The concentrations of platinum are approximately 7 times higher in the feathers examined in this study compared to the levels in eggs, blood and faeces examined in the study by Stevens (1998). Stevens (1998) found significantly higher Pt levels in captive peregrine eggs than in southern peregrine eggs, but in this study Pt levels were slightly higher in the feathers of southern peregrines than in the captive peregrines, although no significant difference could be established. Stevens (1998) found the results unexpected, and the results from this study suggest that they might be erroneous. In the study by Stevens (1998), significantly higher Pt levels were also found in eggs of urban sparrowhawks than in northern and southern wild peregrine eggs. In the present study, however, Pt concentrations are on the same level in both wild peregrines and in urban sparrowhawks, which suggests that Pt concentrations are not increasing in the blood with increasing Pt exposure.

11.2 LA-ICP-MS

Table 15 shows the sample size (number of individuals, feathers and ablations) of feathers analysed by LA-ICP-MS. The number of ablations is the total number of parallel lines shot by the laser on the feathers from the bird in each group.

Table 15. Sample size of feathers analysed by LA-ICP-MS.

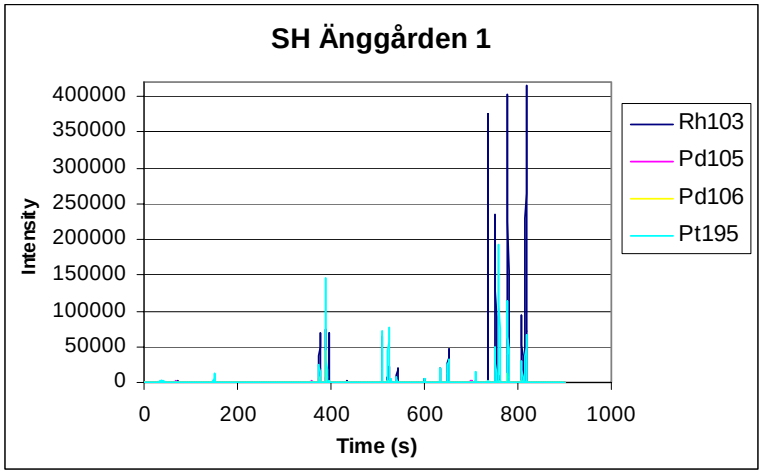
	Number of individuals	Number of feathers	Number of ablations
PF 1982	1	2	6
PF North	2	2	6
PF South	3	4	16
PF Captive	2	2	2
SH City	5	8	35
SH Countryside	5	5	18
Sparrow City	1	1	3
GF North	3	3	3
Grouse North	1	1	1

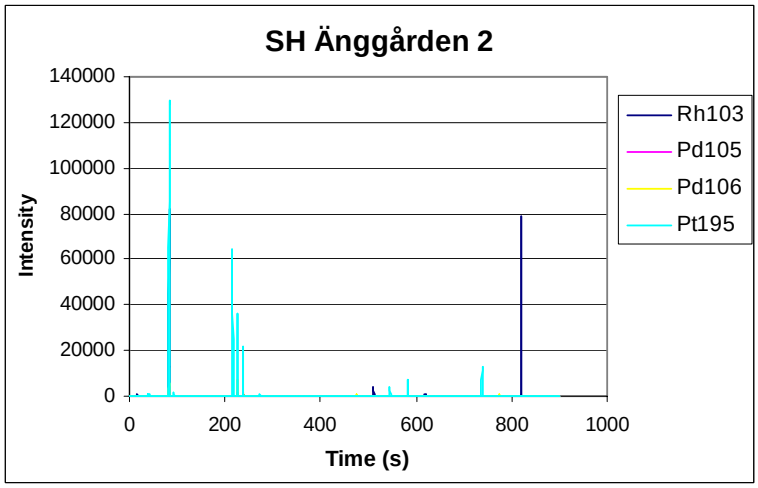
Since feathers grow nearly equally fast in raptors of the same size, data on the growth rate of kestrel feathers were used to estimate feather growth rate of the raptors in this study. Tail-feathers are fully-grown in about 50 days and therefore have a growth rate of approximately 3.7 mm/day. Primaries

form in approximately 45 days and therefore have a growth rate of around 4.4 mm/day (Stresemann and Stresemann, 1960). This information makes it possible to calculate how long time PGM levels were high in the blood during feather formation. The feather is in contact with the blood as it grows, so the time of feather growth that the metal levels are high is the same time that the metal levels were high in the blood, see explanation in chapter 5. The periods with elevated PGM levels are caused by increased PGM concentrations in the blood during this time. The increased blood concentrations might for example be due to ingestion of PGM-contaminated prey, such as sparrows that have been dust bathing close to roads.

The time calculation can be done since the laser shoots a continuous line with a known speed along the shaft of the feather, and since it is known how fast the shaft of the feather grows as described above. The width of the peaks in seconds is recalculated to the corresponding time of feather growth, i.e. the time of high metal levels in the blood. Due to different start times of the ablation, the time scales on the x-axis are not exactly equal to each other in different diagrams. There is a difference of up to 15 seconds between the diagrams. Although it can not be seen in the figures, this has been calculated for when comparing the diagrams and checking if peaks occur at the same time in parallel lines.

Consistent peaks, i.e. peaks that could be found at the same place in the feather shaft several times, were found only in feathers from three individuals. The feathers all





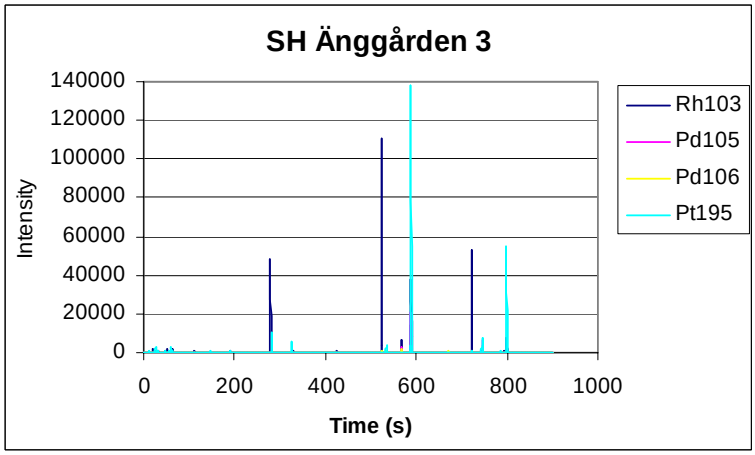


Figure 30. Intensity of PGM signals along the shaft of a sparrowhawk feather (Änggården), using LA-ICP-MS.

come from sparrowhawks in urban areas around Gothenburg; Änggården, Biskopsgården and Axelmossen. Figures 30 and 31 show the intensity or abundance of PGMs along the shaft of a feather from two sparrowhawks living in the city of Gothenburg (Änggården and Biskopsgården). The diagrams were obtained by shooting three parallel and equally long lines along the shaft with the laser (1, 2 and 3). Observe the different intensity scales in the diagrams! Each peak in these diagrams represents around <15-50 minutes of feather growth. 15-50 minutes represents 1-3 registrations by the ICP-MS, respectively. The time range depends on which speed you use for the ablation; a slower speed will give a higher resolution so that one registration (one peak) represents a shorter time period than when going faster.

In figure 30, it is rather clear that the peaks around 600 s. and 800 s. can be detected in all of the parallel lines, meaning that these peaks most probably represent areas where PGMs have been deposited during feather formation. The peaks are rather short though, only around <15-50 minutes, suggesting a fast metabolism of PGMs.

Figure 31, however, shows areas on the shaft that have elevated levels of PGMs during a longer time period in all of the diagrams. All of the parallel lines show high levels of PGMs at 20 s. during a time period that represents about 2 hours of feather growth. There are also high levels of PGMs at 700 s. in diagrams 2 and 3 during a time period that represents about 7-14 hours of feather growth, depending on which diagram you look at. In diagram 1, there is also a peak of Rh and Pd at this time, but it only represents 0.5 hours of feather growth. These wide peaks might suggest, assuming that the

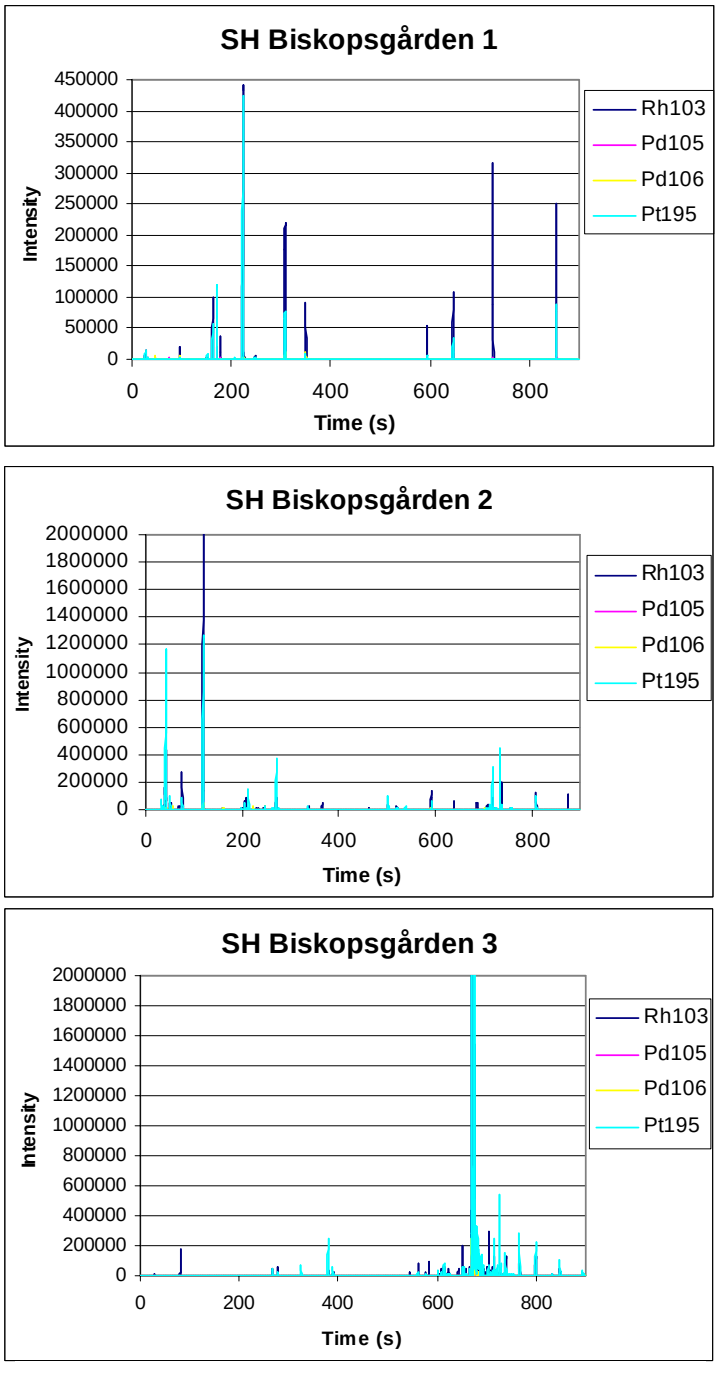


Figure 31. Intensity of PGM signals along the shaft of a sparrowhawk feather (Biskopsgården), using LA-ICP-MS.

metabolism of PGMs is relatively fast (< 1 hour), that PGMs have been supplied continuously to the blood during a longer time, rather than an accidental single exposure.

The diagrams from the laser ablation of a feather from a sparrowhawk living in another part of Gothenburg (Axelmossen) also show high levels of PGMs at two times in all diagrams; around 170-190 s. and around 730-760 s. (figure 32). Observe the different intensity scales in the diagrams! Diagrams 1-4 represent parallel and equally long lines on the feather shaft. The elevated levels at these points might indicate PGMs that were deposited in the feather structure during growth, since they appear in all the parallel ablation lines. The PGM concentrations are higher in the blood for about 1 hour.

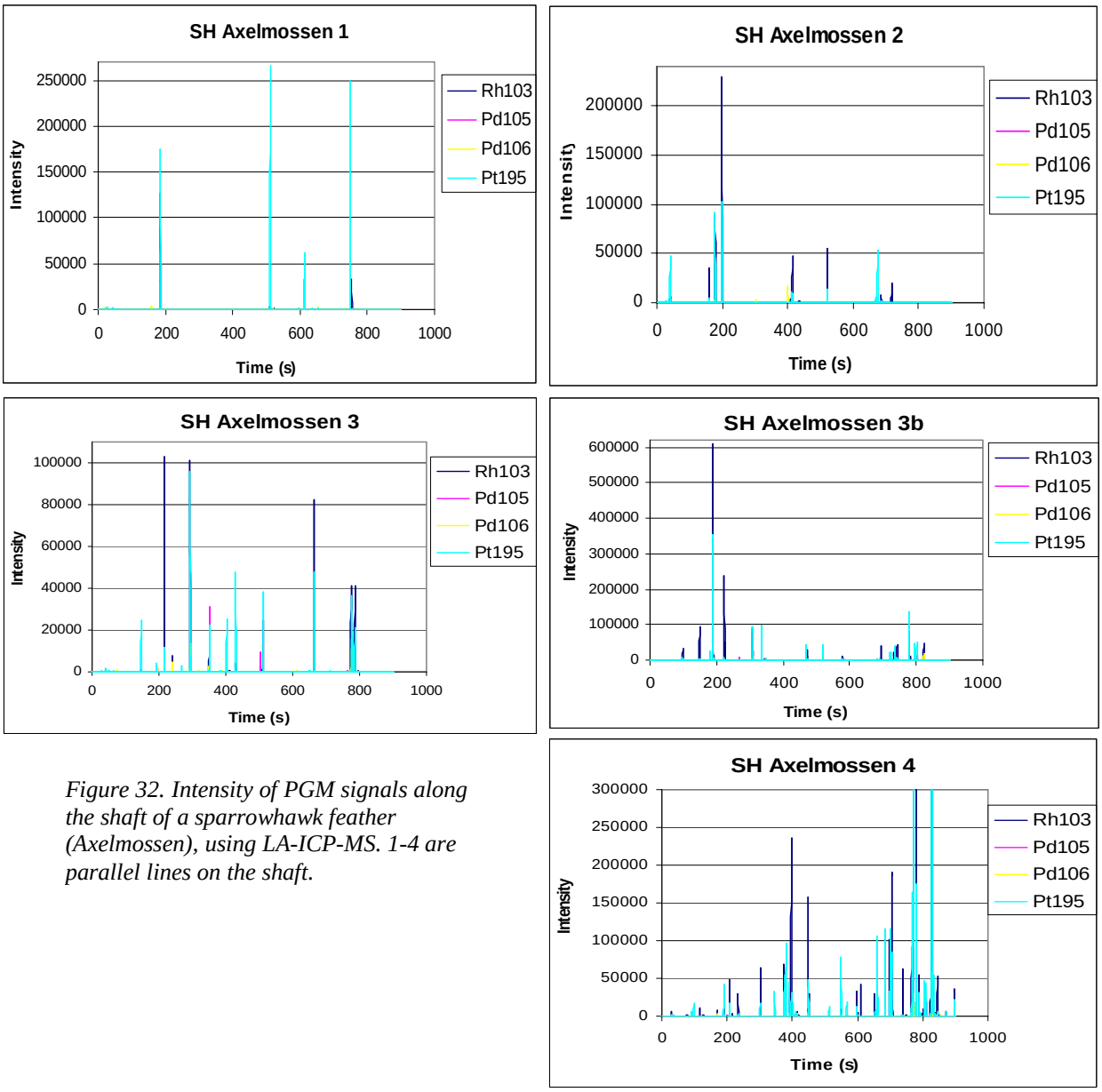


Figure 32. Intensity of PGM signals along the shaft of a sparrowhawk feather (Axelmossen), using LA-ICP-MS. 1-4 are parallel lines on the shaft.

The PGM peaks of about 0.5-2 hours indicate that PGM metabolism is rather quick, the metals do not stay in the blood for a long time. In this time period, PGMs are removed from the bloodstream, possibly transported by proteins in the blood to the liver and the kidney where they accumulate or are further excreted with the faeces. In the liver and the kidneys, PGMs would bind to metallothioneins. Therefore, it would be interesting to investigate liver and kidneys from the raptors in order to determine whether they contain high amounts of PGMs or not. That would give an indication on whether PGMs are bioaccumulating or not.

However, the majority of feathers analysed by LA-ICP-MS did not show this correlation between parallel lines shot by the laser. In all the other feathers examined, no trends for areas with high PGM levels in the feather shafts could be observed. The pattern of PGM intensity in parallel lines always changed in these feathers, so it was not possible to say that the birds had high PGM levels in the blood for a longer period. It is more common that the peaks are shorter and more randomly distributed. These short peaks are merely one or two registrations representing less than 1-15 minutes of feather growth, and that they cannot be detected more than once, even though the same area on the feather is analysed several times by shooting parallel lines on the shaft. This is difficult to explain, but perhaps these random peaks are caused by PGM particles attached randomly on the outside of the feather shaft.

In general, there are more and higher peaks of Rh and Pt than Pd, which is probably due to differences in detection sensitivity between the elements. The detection limits for Pt and Rh are lower than that of Pd.

Ablating a shallow and a deep line in feather shafts can show whether PGMs are attached superficially or inside feathers. If ablating only a very shallow line in the feather, mainly the outside of the feather is analysed. Correspondingly, if ablating a deep line in the feather, also the inside of the feather is analysed. Comparing the graphs from the shallow/deep ablations would make it possible to determine if PGMs are deposited mainly on the outside or mainly inside the feather. This has not been done in this study, but it is a recommendation for further studies. Another way is to compare intact feathers to feather shafts by microwave digestion ICP-MS, the shaft representing mainly internal contamination. This has been done for merely one bird in this study, but more of these kinds of analyses are needed in order to draw conclusions on internal/external contamination.

12. Problems and difficulties

A major problem in ICP-MS analysis is interferences. The signal from interferences often exceeds the PGM signal by a magnitude of two or three.

Figure 37 shows the contribution from interferences on the real PGM concentrations. It is plotted as the ratio of the interference concentration divided by the real PGM concentration on the y-axis, versus different PGM concentrations on the x-axis. Generally, the contribution from interferences to the total concentration is higher the smaller the PGM concentration is, and decreases as the PGM concentration increases. An interference/real concentration ratio below 2 is considered a relatively good result, while a ratio above 3 is not so good.

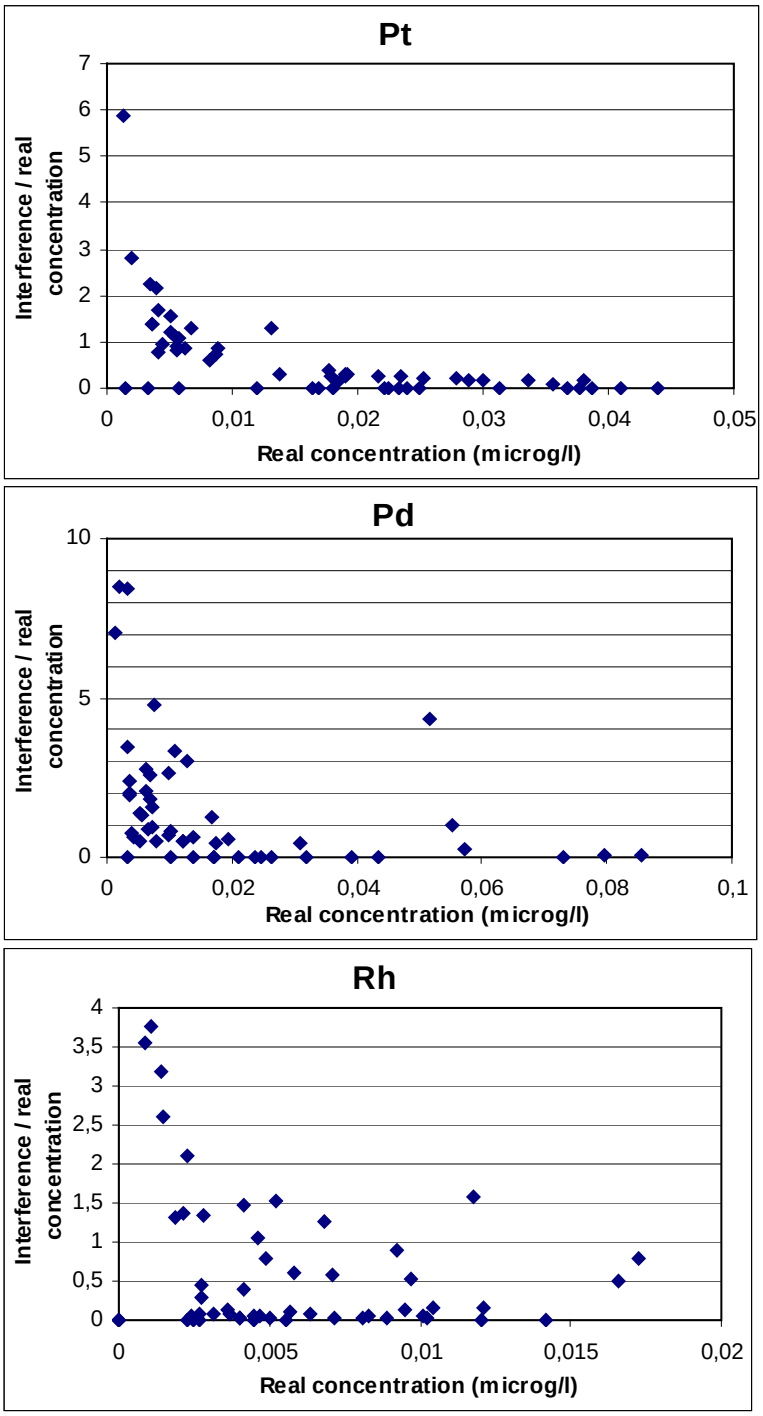


Figure 37. Contribution from interferences on PGM concentrations.

As shown in figure 37, Pt and Rh are the least interfered species of the PGMs analysed. The ratio is seldom higher than 2. Palladium results seem less accurate since interferences often contribute more to the total concentration, at least one-fifth of the concentration values have a ratio of more than 2. Rhodium has a more widespread distribution of the ratios. In some cases, the ratio is higher for a high real concentration than for a low real concentration. However, the ratio is relatively low, most values are below 2. In general, the contribution of interferences to the

total signal is not high, so interferences is not a big problem in the analysis of feathers.

Another problem was the difficulty of interpreting LA-ICP-MS results as discussed previously. It is very time consuming to compare diagrams in order to find peaks occurring at the same time, and it is difficult to explain the occurrence of randomly distributed short peaks.

13. Conclusions

Sparrowhawks living and hunting close to major roads and urbanised areas have higher concentrations of platinum group metals in their feathers than other raptors examined in this study, which are less exposed to PGMs. PGM levels in feathers seemed to follow the decreasing order: SH City > SH Countryside > Sparrow City > Wild PF > PF 1982 > SH Norway > Captive PF > GF > Grouse > PF 1976. However, the sample size was too restricted to make proper statistical calculations and comparisons. The only significant difference in PGM concentrations could be found in Pd and Rh levels between sparrowhawks and captive peregrine falcons. Samples were too few to draw conclusions on the distribution of PGMs in feather shafts and in different feather types and on the difference between female and male peregrines. Results further suggest that PGM concentrations have increased by a factor of around 4-40 since 1976, with the largest increase in the urban sparrowhawk and the lowest in the gyrfalcon. It is also suggested that rhodium and especially palladium are more bioavailable and mobile in the environment than platinum, since platinum levels generally are constant in the feathers, while palladium and rhodium levels generally increase with increasing exposure.

LA-ICP-MS results are rather difficult to interpret, but it seems like platinum group metals in raptors are removed from the blood and metabolised relatively quickly. Generally, within one hour after contamination, PGM levels in the blood are back to initial levels. However, the majority of the peaks are very short, perhaps caused by PGM particles attached to the feather from an outside contamination. Longer time periods of high PGM levels in the feathers, indicating deposition of PGMs in the feather structure from the blood during feather growth, were found only in three urban sparrowhawks.

14. Suggestions

Most important is to collect more feathers for analysis by microwave digestion ICP-MS in order to obtain large enough sample sizes to make statistical calculations. Groups of more than ten individuals in each of the groups examined in this study are desired. Especially, more feathers from birds from

before 1986 need to be analysed. In addition, investigations on PGM levels in eggs, blood and faeces in raptors by microwave digestion ICP-MS should be started. A continuation of this should be to study PGM levels in the liver and the kidneys of raptors, possibly also in prey species such as voles. High levels of inorganic PGMs in the liver might indicate demethylation metabolism of PGMs in raptors. Another interesting thing would be to investigate differences in PGM levels between male and female raptors in wild populations in order to examine the possibility of females sequestering PGMs into eggs. It is also necessary to develop the methodology for LA-ICP-MS in order to simplify interpretation of laser ablation results.

The bioaccumulation potential of platinum group metals should be investigated, particularly for palladium. This could be done by analysing material from each step in a food chain for PGM concentrations and by comparing PGM levels in young and old raptors of the same species living in the same area, for example urban sparrowhawks. The influence of food choice on PGM levels in raptors is also needed for the understanding of uptake mechanisms of platinum group metals. In order to investigate this, PGM levels in kestrels could be compared to those in sparrowhawks. Kestrels mainly feed on small mammals and voles, while sparrowhawks almost exclusively feed on small birds. An English study showed much higher arsenic levels in kestrels than in sparrowhawks, and it has also been shown that small mammals accumulate arsenic (Erry *et al*., 1999). Another study showed higher mercury levels in bird-eating sparrowhawks than in vole-eaters (Solonen *et al*., 1999). It could be possible that small birds and mammals have different amounts of PGMs.

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GLOSSARY

Bronchi = the upper part of the airways.

EC_{50}, LD_{50} or LC_{50} = the concentration of a given substance where 50 % of the exposed subjects die.

Exoskeleton = outer skeleton consisting of chitin.

Ligand = ion or molecule that is bound to a central atom in a complex chemical compound.

Metallothionein = a protein with a low molecular weight which takes part in the regulation of metal concentrations in organisms.

Methioneine = an amino acid, which is a part of a protein.

Nd:YAG = Neodymium-yttrium aluminium garnet ($Y_3Al_5O_{12}$).

Nebulisation = atomisation of a solution into very fine drops.

Appendix

Table 1. Feathers analysed by microwave digestion ICP-MS.

Tube	Bird	Weight (g)	Tube	Bird	Weight (g)
1a	SH Slottskogen	0.0374	1c	SH Strekered	0.0193
2a	SH Blixås	0.0121	2c	SH Duvekärr	0.0225
3a	PF 1982	0.0765	3c	SH Flagsjö V	0.0189
4a	GF SE	0.0362	4c	SH Slottskogen	0.0133
5a	GF N10	0.1066	5c	SH Axelmossen	0.0065
6a	GF SF	0.0622	6c	PF Bohuslän	0.0488
7a	PF Västergötland	0.0906	7c	PF Västergötland	0.046
8a	PF Norrbotten (“Ronja” 0799)	0.0358	8c	GF SE	0.0379
9a	PF Captive female	0.0667	9c	GF SF	0.0931
10a	PF Captive male	0.0472	10c	GF N10	0.1134
11a	Sparrow Axlemossen (2 in 1)	0.0128	11c	SH Tuve (tail)	0.019
12a	Sparrow Axlemossen (intact)	0.0148	12c	SH Tuve (wing)	0.0386
13a	Grouse Sarek	0.0163	13c	SH Tuve (neck)	0.0015
14a	SH Axlemossen (intact)	0.0315	14c	SH Tuve (belly)	0.0017
1b	PF Captive female, no.116	0.1814	1d	SH SW Norway, Flåta	0.0265
2b	PF Captive male, no.42	0.1647	2d	SH SW Norway, Vegårshei	0.0295
3b	PF Captive female, no.122	0.0551	3d	PF Captive male, no. 38, p. 1	0.0447
4b	PF Captive male, no.64	0.0425	4d	PF Captive male, no. 38, p. 2	0.062
5b	PF Captive male, no.388	0.1105	5d	PF Captive male, no. 38, p. 3	0.0497
6b	PF Captive female, no.101	0.053	6d	PF Captive male, no.38, p. 4	0.0437
7b	PF Captive male, no.120	0.0454	7d	PF Captive male, no.38, p. 5	0.0353
8b	PF Captive female, no.223	0.0556	8d	PF Captive male, no.38, p. 6	0.0261
9b	PF Captive male, no.349	0.0395	9d	PF Captive male, no.38, p. 7	0.0198
10b	PF Captive female, no.377	0.119	10d	PF Captive male, no.38, p. 8	0.015
11b	PF 1976, Scotland (tail)	0.066	11d	PF Captive male, no.38, p. 9	0.0093
12b	PF 1976, Scotland (primary)	0.1457	12d	PF Captive male, no.38, p. 10	0.0054
13b	Grouse Sarek	0.0568	13d	PF Captive male, no.38, p. 11	0.0005
14b	Grouse Västerbotten	0.0269	14d	PF 1976, Scotland	0.103

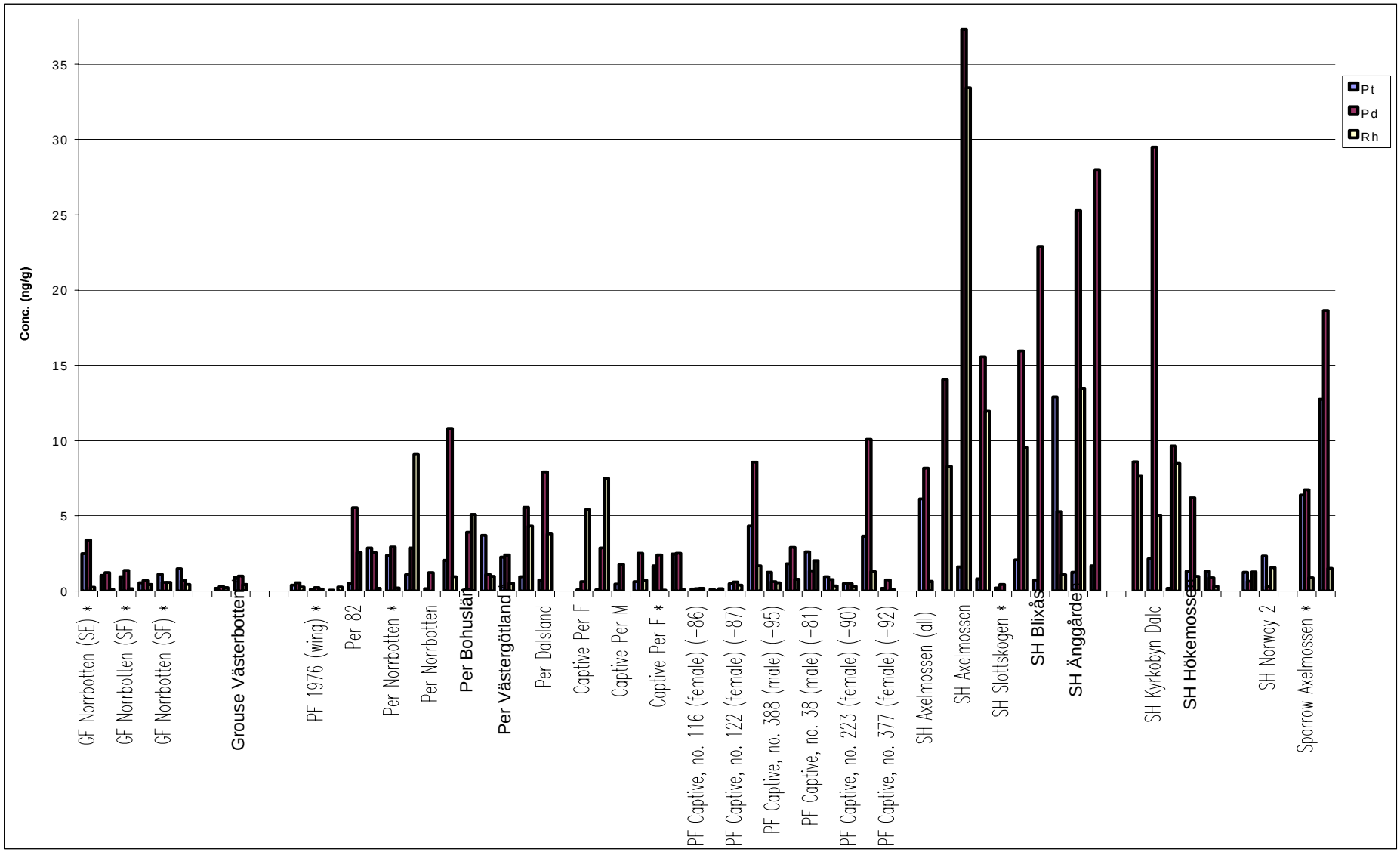

Figure 1. PGM concentration obtained by ICP-MS after microwave digestion in all feather samples.