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Platinum Group Elements in the Feathers of Raptors and Their Prey

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Abstract. Platinum (Pt), palladium (Pd), and rhodium (Rh) concentrations were determined in the feathers of three raptor species in Sweden, the sparrowhawk (*Accipiter nisus*), the peregrine falcon (*Falco peregrinus*), and the gyrfalcon (*Falco rusticolus*), as well as the main prey of the sparrowhawk (the house sparrow, *Passer domesticus*) and the gyrfalcon (the willow grouse, *Lagopus lagopus*). The analysis of feathers from 1917–1999 revealed a clear temporal trend, with significantly higher Rh concentrations in sparrowhawk and peregrine falcon after 1986. There is evidence for increasing platinum group element (PGE) concentrations from 1917 to 1999 in peregrine falcon and sparrowhawk. This suggests that feathers reflect increased PGE concentrations in the environment over this time period. Mean concentrations of PGE in feathers of raptors after 1986 ranged from 0.3 to 1.8 ng g^{-1} for Pt, 0.6 to 2.1 ng g^{-1} for Pd (indicative values), and 0.1 to 0.6 ng g^{-1} for Rh. House sparrows in urban areas had significantly higher Pt and Pd concentrations than urban sparrowhawks. The higher Pd concentrations in relation to Pt and Rh may indicate the greater mobility of Pd in the environment. Although PGE concentrations are generally higher in birds living in urban areas, no significant spatial trend could be established. This is partly due to the widespread distribution of automobiles and partly because birds forage and integrate PGE exposure over large areas. Laser ablation analysis demonstrates that PGE contamination of feathers is predominantly external, consisting of small particles in the nanometer size range. Other indications of external contamination are that Pt and Pd levels are significantly higher in the vane than in the shaft and that PGE relative ratios (except Pd) reflect urban particles.

The three platinum group elements (PGE) used in automobile catalysts—platinum (Pt), palladium (Pd), and rhodium (Rh)—occur naturally at very low levels, but concentrations have been increasing in the urban environment (Wei and Morrison 1994; Schäfer *et al.* 1999; Rauch and Morrison 2001). Automobile catalysts were first introduced in the United States and Japan in 1975–1976 and have been mandatory in Sweden since 1989 and in the European Union since 1993. In 1986, few cars in Sweden were equipped with catalytic converters, whereas in 1989, the share of exhaust catalyst equipped cars in Sweden was close to 30%. On road, metallic PGE particles in the micro- and submicrometer range with a low soluble fraction are emitted from the automobile catalyst due to surface abrasion of the washcoat (Moldovan *et al.* 1999; Palacios *et al.* 2000a, 2000b). Emission rates from aged gasoline catalysts of 6–8 ng km^{-1} for Pt, 12–16 ng km^{-1} for Pd, and 4–12 ng km^{-1} for Rh, with 108–150 ng Pt km^{-1} for aged diesel catalysts, have recently been reported (Palacios *et al.* 2000a). Elevated PGE concentrations have been found in airborne particles (Alt *et al.* 1993; Rauch *et al.* 2001a; Zereini *et al.* 2001), road dust (Wei and Morrison 1994; Farago *et al.* 1996), roadside soil (Schäfer and Puchelt 1998; Zereini *et al.* 1999), river sediment (Rauch *et al.* 2000b), sewage sludge (Schäfer *et al.* 1999), roadside grass (Helmers and Mergel 1998), and even in Greenland snow (Barbante *et al.* 2001). Until recently, it was believed that PGEs are relatively inert, but it has now been shown that these metals undergo environmental transformations into more reactive species (Lustig *et al.* 1996, 1997, 1998; Rauch and Morrison 2000). The toxicity of Pt has been investigated in detail (Lindell 1997), but less is known about Pd and Rh. Recently, Pd has been increasingly favored over Pt as the catalytic metal for oxidation in automobile catalysts (Johnson Matthey 1996; Palacios *et al.* 2000a, 2000b). This is a concern because it has been shown that Pd is more mobile in the environment than either Pt or Rh (Schäfer *et al.* 1998; Jarvis *et al.* 2001; Moldovan *et al.* 2001). There is a need for more knowledge about the transformations and transport routes of PGEs in the environment, as well as their potential accumulation in organisms.

Birds are useful bioindicators because they integrate temporal and spatial exposure (Burger 1993). Metals can be both externally attached and internally deposited in the feather structure during feather growth. Feathers are easy to collect and store, and feather sampling is noninvasive. It is also possible to study historical changes in feather metal concentrations, because metal profiles in feathers are stable with time (Berg *et al.* 1966; Appelquist *et al.* 1984; Goede and de Bruin 1984; Burger 1993).

During feather growth, the shaft contains an axial artery (Lucas and Stettenheim 1972). Many heavy metals carried with

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the blood in the artery, particularly mercury, are sequestered into the feather by binding to sulfhydryl groups in the feather keratin structure when the feather is growing (Crewther *et al.* 1965; Goede and de Bruin 1984). When the feather is fully formed, the blood flow through the artery ceases. Thus feather metal concentrations due to internal exposure originate from circulating blood during feather growth (Goede *et al.* 1989; Burger and Gochfeld 1997). A raptor primary or rectrice is fully grown in about 45–50 days, but the sequence and timing of molt depends on species and migration pattern. The raptor species studied here replace all primaries, secondaries, and rectrices once a year, mainly during summer. The feathers analyzed can therefore be accurately dated to year of feather growth.

The uptake mechanisms for metals in feathers are inhalation of airborne particles, dry or wet deposition, contamination through direct contact with the environment (water, soil, or vegetation), preening, and ingestion of contaminated prey. Most raptors ingest the feathers, furs, and bones of their prey and discard excess material as pellets.

Metals can be lost from feathers through precipitation, bathing in water, and rubbing (Goede and de Bruin 1986; Weyers *et al.* 1988). Goede and de Bruin (1984) recommend using the shaft only when analyzing molted feathers, because it is subject to less external contamination than the vane. The use of feathers requires consideration of whether metal deposition in feathers represents recent exposure or mobilization from storage in other body tissues and variation of metal levels within feathers and between feather types (Burger 1993). Furness *et al.* (1986) found that metal levels in blood reflect current exposure through dietary intake as well as exposure from metals stored in internal tissues from which they are mobilized when the feather is growing.

Pt and Rh can be successfully determined by a catalytic procedure of cathodic stripping voltammetry (CSV) (Wei and Morrison 1994; León *et al.* 1997), but this technique does not allow Pd analysis at environmentally relevant concentrations and is particularly prone to organic interferences. ICP-MS (inductively coupled plasma–mass spectrometry) has become the method of choice for the determination of PGE in environmental samples because it provides sufficiently low detection limits and allows the simultaneous determination of Pd, Pt, and Rh. However, spectral interferences are a well-known problem in the determination of PGE by ICP-MS (Barbante *et al.* 1999; Rauch *et al.* 2000b; Moldovan *et al.* 2001), although they can be corrected mathematically (Parent *et al.* 1997; Rauch *et al.* 2001a; Moldovan *et al.* 1999, 2001). A recent advance is laser ablation sampling for ICP-MS, which provides the possibility for micrometric resolution of PGE in bird feathers (Rauch *et al.* 2000a, 2001b).

In this study, Pt, Pd, and Rh concentrations were determined in the feathers of sparrowhawk (*Accipiter nisus*), peregrine falcon (*Falco peregrinus*), gyrfalcon (*Falco rusticolus*), willow grouse (*Lagopus lagopus*), and house sparrow (*Passer domesticus*), collected either as molted feathers in breeding territories or sampled from captive or dead birds. The raptors studied have different food choice, habitat, and migration patterns. A temporal trend was investigated by sampling from museum collections of stuffed birds. The aim of this article is to determine whether the increasing use of PGEs in automobile catalysts has affected the temporal and spatial patterns of PGE concentrations in raptor feathers.

Materials and Methods

Collection of Feathers

PGE concentrations were determined in the feathers of three raptor species from different parts of Sweden (the sparrowhawk, peregrine falcon, and gyrfalcon). Two prey species were analyzed (the house sparrow, taken by sparrowhawks, and the willow grouse, preyed on by gyrfalcons).

Sparrowhawks were divided into urban and rural sparrowhawks depending on the location of their nest in relation to urban and rural areas in the city of Göteborg, southwest Sweden. Sparrowhawks breeding in parks and forests within the city of Göteborg were classified as urban, and sparrowhawks breeding in large forests in the countryside 15–30 km outside the city border were classified as rural. The sparrowhawk feeds mainly on passerines, and a common prey species is the house sparrow (Newton 1986; Götmark and Post 1996). Because the sparrow lives in the direct vicinity of urbanization and bathes in road dust, it could contain relatively high levels of PGEs. It is likely that dust bathing causes dust particles containing PGEs to attach to the feather vane. In addition, sparrowhawk feathers from 1939 to 1996 were analyzed to determine the temporal trend of PGE concentrations in feathers.

Wild peregrine falcons from south and north Sweden were selected to study the influence of different food chains on PGE concentrations. The northern peregrine falcons hunt aquatic bird species, such as waders, whereas the southern peregrine falcons feed on birds belonging to a terrestrial food chain (Lindberg and Odsjö 1983). Both populations migrate to south west Europe and spend the winter in coastal and agricultural areas, estuaries, and river valleys. Feathers from captive peregrine falcons, held at a breeding station outside Göteborg, were used as a control group. These falcons are fed on raised chickens. Wild peregrine falcon feathers from 1917 to 1999 were selected to determine the temporal trend of PGE concentrations.

The gyrfalcon was selected because it is sedentary, the habitat being mountain areas in north Sweden, far from urbanization. The main prey of the gyrfalcon, the willow grouse, is a sedentary herbivore (Lindberg 1983).

Molted sparrowhawk flight feathers were collected in March–October 1991–1997 at nest sites in urban and rural areas around Göteborg. Feathers from house sparrows were collected in April–June 1997–1998 in urban areas in Göteborg. Molted feathers, mainly primaries and rectrices, from wild peregrine falcons were collected at nest sites in May–July 1998–2000 in southwest Sweden (latitude 58–59° N) and in north Sweden (latitude 65–68° N). Captive peregrine falcon feathers were collected in November 1999. Molted feathers from gyrfalcon were collected in June 1999 at nest sites in remote areas in north Sweden (latitude 65–68° N) as well as feathers from the main prey, the willow grouse. Feathers from sparrowhawks, found 1939–1996 in urban and rural areas around Göteborg, and wild peregrine falcons, found 1918–1994 in south Sweden, were selected from a collection of stuffed birds at the Museum of Natural History, Göteborg, in January 2001. In addition, a number of feathers were taken from dead, frozen birds. The type of feather and its position in the molt sequence were determined. Feathers were stored in polyethylene bags at room temperature.

Feather Analysis

Only the shaft was used for analysis of PGE concentrations in bird groups to avoid influence from excessive external PGE contamination

(Goede and de Bruin 1984). Shafts from unwashed feathers were used because no significant difference was found between unwashed and washed feathers.

The whole shaft was used because concentrations might vary in different parts of the shaft (Berg *et al.* 1966). The vane was removed with stainless steel scissors and a small section of the shaft (~ 0.5 cm) was detached at the shaft base; this avoids blood residuals. It was assumed that total PGE concentrations in molted feathers do not alter with time during storage, as for mercury (Appelquist *et al.* 1984).

The origin of PGE contamination (external/internal) was investigated by washing and comparing vane and shaft PGE concentrations and by laser ablation ICP-MS. For the washing, one primary and two rectrices from an urban sparrowhawk were divided into two parts along the shaft. One part was washed in 0.01% Triton X-100 in an ultrasonic bath at 40°C for 15 min (Altmeyer *et al.* 1991). The vane was clipped from the shaft with stainless steel scissors, and the shaft and vane from unwashed and washed feathers were analyzed separately.

Digestion. Samples were weighed and placed in acid-washed and sealed PTFE digestion vessels (HP500), followed by mineralization in a microwave digestion system (CEM Mars5). Digestion was in 8-ml *aqua regia* (1:3, HNO_3:HCl). Suprapure grade subdistilled 65% HNO_3 and 30% HCl (Promochem AB, Ulricehamn, Sweden) were used. The microwave digestion followed a program reaching a maximum temperature of 210°C and a maximum pressure of 150 psi in 30 min (Moldovan *et al.* 2001). Samples were heated to dryness on a hot plate, and residues were redissolved in 5 ml of 2% hydrochloric acid.

Laboratory Reference Material. No suitable certified reference material (CRM) exists for trace PGEs in biological materials. Consequently, two sets of laboratory reference materials (LRMs) were prepared by grinding whole feathers from captive peregrine falcons and house sparrow, respectively, into a fine powder. The LRM was analyzed together with each batch of samples.

ICP-MS Analysis. Analysis was carried out by ICP-MS (Perkin Elmer Elan 6000) with pneumatic nebulization. Settings for the ICP-MS are presented in Table 1. LRM was included in each batch of samples to indicate accuracy. In and Ir were used as internal standard. Detection limits of 0.6 ng L^{-1} for Pt, 3.3 ng L^{-1} for Pd, and 0.9 ng L^{-1} for Rh have been reported for quadrupole ICP-MS (Gómez *et al.* 2000a).

Interference is a severe obstacle in the determination of trace PGE concentrations by ICP-MS. The predominant interfering species are $ArCu^+$, YO^+, SrO^+, and RbO^+ for Pd; HfO^+ for Pt; and $ArCu^+$, Pb^{2+}, SrO^+, and RbO^+ for Rh. Most of these interferences cannot be resolved through mass/charge ratio, even with a sector field instrument, and therefore a mathematical correction is required to determine PGE concentrations (Equations 1–3) (Moldovan *et al.* 2001; Rauch *et al.* 2001a).

$$I_{Pt} = I_{Pt,s} - (I_{i,s} \times R_{HfO}) \qquad (1)$$

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

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

where I_{Pt} = the corrected Pt signal, $I_{Pt,s}$ = the Pt signal measured for the sample solution, $I_{i,s}$ = the interference signal in the sample solution, and R_{HfO} = the previously determined HfO^+/Hf signal ratio.

R_{HfO} is determined from interference standard solutions, with the same nomenclature for *R* and *I* applying to equations 2 and 3. The relative contribution of interferences to the PGE signal was calculated as the ratio of the total concentration of interferences and the corrected PGE concentration. The interference/corrected concentration as a function of the corrected concentration for digested feathers is presented in Figure 1. At a ratio of one, half the signal is due to interferences, and the other half originates from the PGE in the sample. At a ratio lower than one, PGE concentrations can be accurately determined with mathematical concentration, whereas ratios higher than one need careful estimation of interference and calculation. Ratios are in many cases high for feather samples, 49% of the samples analyzed had a ratio higher than one for Pt, 76% for Pd, and 19% for Rh. Generally, the ratio decreased as the corrected concentration increased. Determination of Pd by ICP-MS is known to be difficult (Rauch *et al.* 2000b), and Pd results in the present study can only be considered indicative. Concentrations with an interference ratio higher than five were not used (Figure 1).

Table 1. Settings for ICP-MS for the analysis of PGE in digested feathers

Sample introduction	
Sample uptake	1 ml min^{-1}
Nebulizer	Cross flow
Nebulizer gas	Argon, 0.86 L min^{-1}
ICP	
RF power	1,000 W
Plasma gas	Argon, 16 L min^{-1}
Auxiliary gas	Argon, 0.9 L min^{-1}
Cones	Nickel
Acquisition	
Analytes scanned	^{103}Rh, ^{105}Pd, ^{106}Pd, ^{195}Pt
Data acquisition	Peak hopping
Dwell time	100 ms
Sweeps per reading	10
Readings per replicate	1
Replicates	6

As PGEs are present at trace concentrations in feathers (often close to the detection limit), and because interference correction is difficult for low concentrations, especially for Pd, some results were below zero after mathematical correction. Depending on the reason for the negative values, they were either removed (when interferences were clearly very high) or defined as below the detection limit (when initial PGE concentrations were very low).

Laser Ablation ICP-MS Analysis. Laser ablation ICP-MS was used to investigate the distribution pattern of PGE along feather shafts. A line was ablated along the shaft of primaries and rectrices from sparrowhawk, peregrine falcon, gyrfalcon, grouse, and house sparrow. In total, feathers from seven sparrowhawks, six peregrine falcons, and one individual each of gyrfalcon, grouse, and house sparrow were used. The ablated material was swept to the ICP-MS by argon gas for analysis. Table 2 shows the settings for the laser ablation. The dwell time is the time it takes to analyze one element. Because the shaft differs in hardness between species, the laser energy level was optimized according to the type of feather to not shoot through the shaft. For the comparison of number of peaks between different birds, a scan speed of 50 μm s^{-1} was used to obtain a large number of peaks. A low scan speed of 5 μm s^{-1} was used for the determination of PGE particle sizes because it provides a high resolution.

The advantage of laser ablation as a sample introduction system is the possibility for micrometric sampling and the greatly reduced oxide interference. Decreases in intensity of up to two orders of magnitude for a number of O-, N-, H-, and Ar-containing species has been observed (Evans and Giglio 1999), and lower interference have been observed for the determination of PGE by laser ablation ICP-MS (Motelica-Heino *et al.* 2001). In addition, laser ablation allows for the

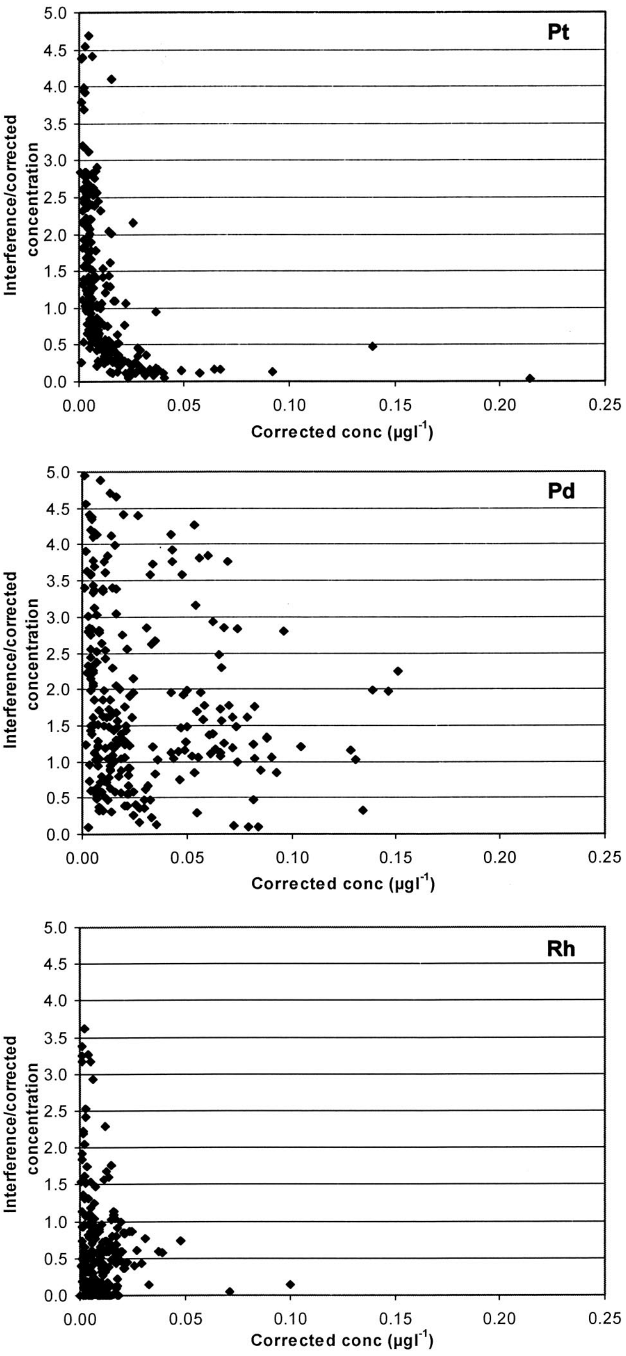

Fig. 1. Interference/corrected concentration versus corrected concentration for Pt, Pd, and Rh in solutions obtained from digestion of feathers. Corrected concentrations were calculated from Equations 1–3. Results are expressed in µg L^{-1} to provide analytical interference

direct analysis of solid samples, which reduces the potential for contamination during sample digestion.

Statistics

Statistical analyses were performed using the Mann-Whitney U-test and linear regression (Siegel and Castellan 1988). The significance level is expressed as $p < 0.05$. Mean and standard error of the mean (SE) is presented as mean ± SE.

Table 2. Instrumental settings for laser ablation of bird feathers when coupled to ICP-MS

Laser ablation	
Ablation type	Single line scan
Carrier gas	Argon, 1 L min^{-1}
Operating mode	Q-switch
Pulse width	< 6 ns
Spot size	200 µm
Laser energy level	2–3 mJ
Repetition rate of laser pulse	20 Hz
Scan speed	5 and 50 µm s^{-1}
Acquisition	
Analytes scanned	^{103}Rh, ^{105}Pd, ^{106}Pd, ^{195}Pt, ^{206}Pb, ^{140}Ce
Data aquisition	Peak hopping
Dwell time	1–3 ms

Results and Discussion

PGE Concentrations in Feathers

Accuracy of Feather Analysis. PGE concentrations in the LRM were on the same level in all batches analyzed, thereby certifying the relative accuracy of the results (Table 3). PGE levels are higher in the LRM than in other samples. This is probably because the vane was also used in the LRM, but only the shaft was used in the other samples.

Temporal Trends. An increasing temporal trend was observed for PGEs in feathers, suggesting increasing PGE levels in raptors since the introduction of automobile catalysts to Sweden in 1986. PGE concentrations were higher in peregrine falcons from 1989–1999 compared to peregrine falcons from 1917–1982. There was a significant difference for Rh ($p < 0.01$), but not for Pt and Pd. Linear regression revealed an increasing trend in PGE concentrations from 1917 to 1999, although this was not significant due to the limited sample size (Figure 2).

Linear regression also showed an increasing trend in PGE concentrations in sparrowhawks from 1939 to 1996, although this was not statistically significant (Figure 3). PGE concentrations were higher in sparrowhawks from 1988–1996 compared to sparrowhawks from 1939–1986. For Rh, the difference was significant ($p < 0.005$), but not for Pt and Pd.

Spatial Trends and Bird Group Comparisons. Results for PGE concentrations in feathers of the different bird groups are summarized and illustrated in Figure 4. Because no significant difference was found in metal levels between urban and rural sparrowhawks, and because the division of urban and rural habitats is rather subjective (particularly because the birds hunt over large areas and often move from rural to urban habitats during winter), urban and rural sparrowhawk results are combined.

The highest Pt concentration of 1.8 ng g^{-1} was found in

Table 3. Mean Pt, Pd, and Rh concentrations ± SE in the LRMs (n is the number of samples)

	PGE ($ng\ g^{-1}$)					
LRM	Pt	n	Pd*	n	Rh	n
Captive peregrine falcon	0.99 ± 0.11	12	2.74 ± 0.23	7	0.54 ± 0.06	13
House sparrow	1.46 ± 0.18	9	3.89 ± 0.56	5	0.54 ± 0.06	9

* Indicative.

feathers of the urban sparrowhawk. A concentration of 1.1 ng g^{-1} was found in the captive peregrine, and the rural sparrowhawk had 0.8 ng g^{-1}. The Pt concentration in the gyrfalcon and the grouse was around 0.65 ng g^{-1}, and the sparrowhawks from before 1986 and southern wild peregrine falcons had 0.5 ng g^{-1}. The peregrine falcons from before 1986 and the northern wild peregrine had the lowest Pt levels of 0.3 ng g^{-1} and 0.25 ng g^{-1}, respectively (Figure 4).

The Pd concentration was highest in the urban sparrowhawk and the captive peregrine falcon, 2.1 ng g^{-1}. The southern wild peregrine falcon had 1.4 ng g^{-1}. The rural sparrowhawk, the northern wild peregrine falcon, and the grouse had 0.9–1.0 ng g^{-1}. The gyrfalcon and sparrowhawks from before 1986 had around 0.6 ng g^{-1}; the lowest Pd concentration of 0.5 ng g^{-1} was found in peregrine falcons from before 1986 (Figure 4). Pd concentrations are consistently higher than Pt and Rh concentrations, indicating an additional uptake mechanism for Pd, *e.g.*, internal contamination.

The highest Rh level of 0.6 ng g^{-1} was found in the urban sparrowhawk. In the rural sparrowhawk and the captive peregrine falcon Rh was close to 0.45 ng g^{-1}. The general Rh level was 0.3 ng g^{-1} in the southern wild peregrine, the northern wild peregrine, sparrowhawks from before 1986, the gyrfalcon, and the grouse. The lowest Rh concentration of 0.1 ng g^{-1} was found in wild peregrine falcons from before 1986 (Figure 4).

No significant difference was found in PGE concentrations between northern and southern wild peregrine falcons, suggesting that there is no difference between a terrestrial and an aquatic food chain (Figure 4).

Pt and Pd concentrations were significantly higher in the feather shafts of the house sparrow ($p < 0.005$) compared to the sparrowhawk, whereas Rh concentrations were significantly higher in the sparrowhawk ($p < 0.05$) (Table 4). The higher Pt and Pd concentrations in house sparrows are probably due to their living close to the ground and traffic, for example, taking dust baths and eating grains in contaminated road dust. Thus, house sparrows are exposed to high PGE concentrations, with the possibility of both external and internal contamination.

In general, spatial differences were not found to be statistically significant. This is partly due to the widespread distribution of automobiles and partly because birds forage and integrate PGE exposure over large areas and in some cases due to a limited sample size. However, the relatively high PGE concentrations in captive peregrine falcons were unexpected.

The relatively high standard errors are probably due to the distribution pattern of PGE in feathers. It is suggested that Pt, Rh, and, in part, Pd contamination is in the form of external randomly attached particles, and therefore, feather concentrations might vary even within feathers of the same individual, depending on the presence of external particles on different feathers.

Identification of Source of PGE Contamination for Feathers

Feather Washing. One approach to investigating the origin of feather contamination is to compare washed and unwashed feathers and to compare concentrations in shaft and vane. The vane is assumed to contain higher relative concentrations of externally bound metals because particles are more easily trapped in the vane than in the shaft (Goede and de Bruin 1984). Hg concentrations in both shaft and vane reflect internal deposition only; As, Pb, and Se concentrations in the shaft reflect internal deposition, whereas vane concentrations also reflect external deposition (Goede and de Bruin 1984). If the greater proportion of contamination is external, then washing should lead to lowered vane concentrations.

No significant difference in shaft and vane PGE concentrations was found between unwashed and washed feathers. However, it has been shown that it is very difficult to wash particles from feathers, particularly if the particles are very small. Electron-microscope photographs showed that external Pb, Zn, and Cd particles in a μm size range cannot be completely removed by washing feathers in 1% Triton X-100 and propanone in an ultrasonic bath for 3 h (Weyers *et al.* 1988). Edwards and Smith (1984) compared mineral profiles of feathers washed with deionized water and feathers washed with 1% Triton X-100 and found significantly lower concentrations of Ca and Mg only.

The vane had significantly higher concentrations of Pt and Pd than the shaft ($p < 0.05$), an indication of external contamination (Goede and de Bruin 1984).

PGE Distribution Along Feathers. Figure 5 shows typical laser ablation feather scans for PGEs (^{195}Pt, ^{103}Rh, ^{105}Pd) and ^{206}Pb, for a rural sparrowhawk feather. PGE intensities have been normalized for isotopic abundance. Interferences were not corrected for in laser ablation ICP-MS analysis. Interfering elements were measured on several samples together with PGE, and increasing signal for interferents were not found to result in a PGE peak. PGE peaks were generally sharp, with a few high peaks randomly distributed along the shaft, and metals were usually not detected more than once in the same place. Individual PGE were usually detected, rather than two or all three PGEs occurring at the same spot. This heterogeneous distribution of PGE along the shaft indicates external contamination by PGE containing particles. The presence of single PGE is related to limitations of laser ablation ICP-MS due to the occurrence of PGEs in small particles, with diameters in the range 5–15 nm, and relatively low concentrations. A few larger particles (2.5–5 μm) were found. Approximately 85% of the peaks represent one PGE alone, *i.e.*, particles of 5–15 nm size.

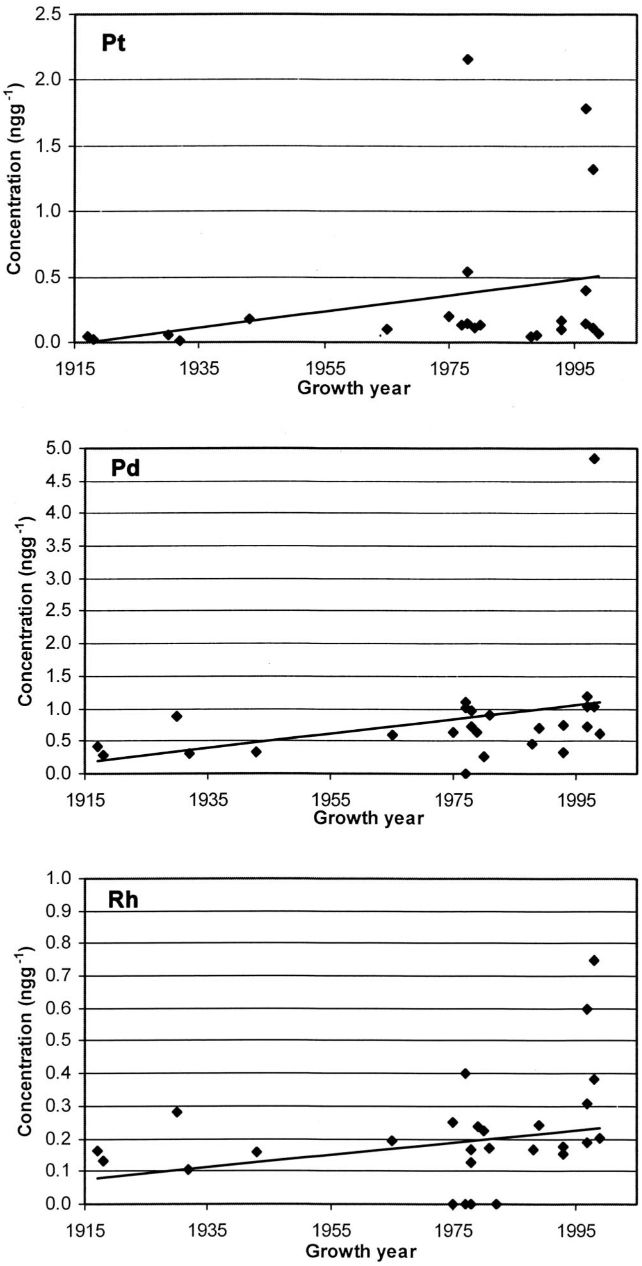

Fig. 2. Mean PGE concentrations in wild peregrine falcon from 1917 to 1999. Each point represents one individual. A linear regression trendline has been applied to the data points

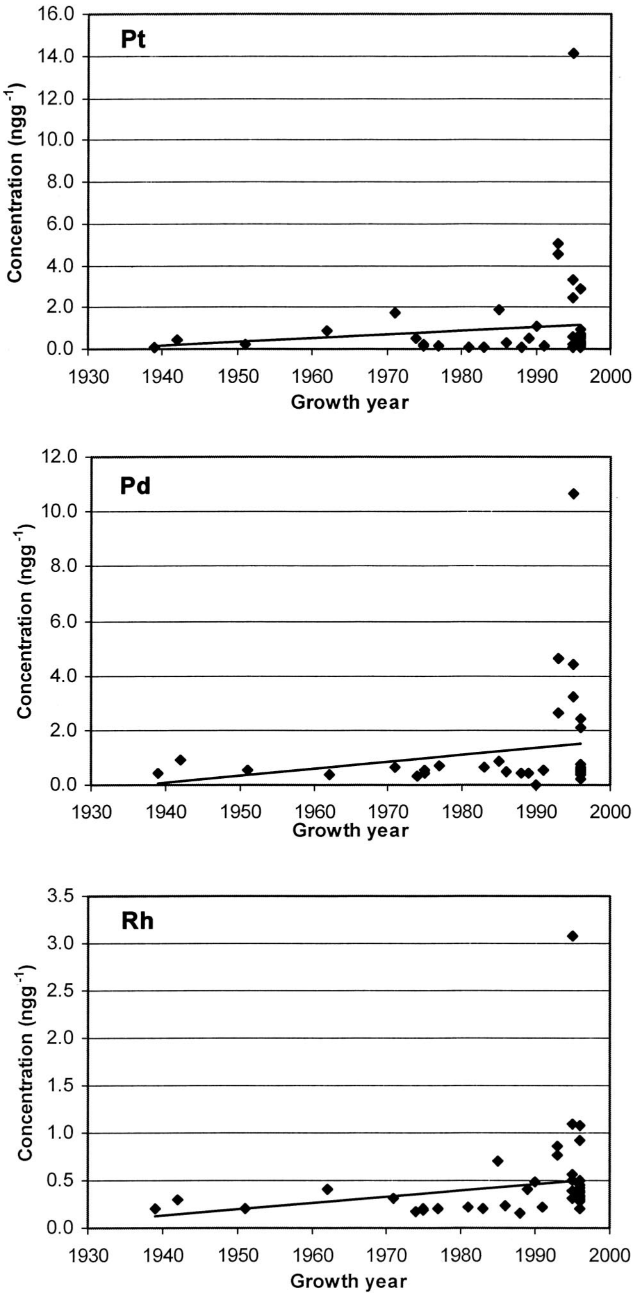

Fig. 3. Mean PGE concentrations in sparrowhawk from 1939 to 1996. Each point represents one individual. A linear regression trend line has been applied to the data points

External PGE contamination is further suggested by the occurrence of Ce together with PGE (Rauch *et al.* 2001a). The possibility to measure Ce together with PGE is the result of the relatively high Ce concentration in PGEs containing particles, as indicated by the high signal measured for Ce peaks. Ce is a major component of the catalyst, and it has recently been demonstrated that Ce could be used to trace PGE containing particles in the environment (Rauch *et al.* 2000a).

The importance of small urban particles has been shown previously. Pt concentrations were highest in airborne particles of the smallest size fraction studied, < 0.39 μm (Gómez *et al.* 2000b), and another study demonstrated higher Pt concentrations in small airborne particles (0.5–8 μm) than in particles $>$ 8 μm (Alt *et al.* 1993). In road dust, PGE concentrations are higher in the $<$ 63 μm fraction than in the 63–250 μm fraction (Rauch 2001).

The number of PGE peaks (*i.e.*, external particles) per ablated cm on the feather shaft was compared between different bird groups. The sparrowhawk had the highest number of peaks, and the number of peaks as compared between the bird groups correlated with PGE concentrations measured by ICP-MS.

The occurrence of Pb in feathers is due to both internal and

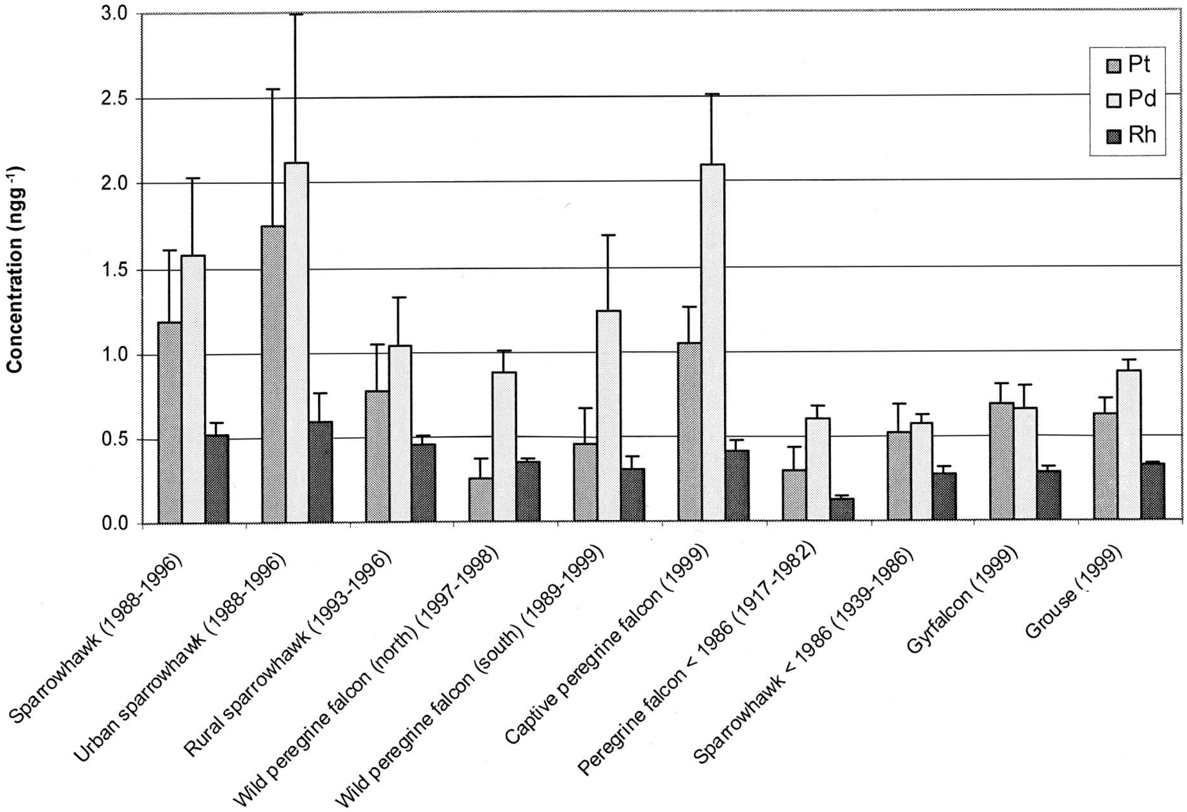

Fig. 4. Mean PGE concentrations in flight feathers from sparrowhawk, peregrine falcon, gyrfalcon, and grouse. Bars represent standard errors of the mean. The year of collection is written in parenthesis. Number of samples were (depending on element analyzed) sparrowhawk, 38 (Pt), 27 (Pd), 41 (Rh); urban sparrowhawk, 21 (Pt), 13 (Pd), 18 (Rh); rural sparrowhawk, 17 (Pt), 14 (Pd), 23 (Rh); wild peregrine falcon (north), 3 (Pt, Pd, Rh); wild peregrine falcon (south), 11 (Pt, Pd, Rh); captive peregrine falcon, 40 (Pt), 43 (Pd), 44 (Rh); peregrine falcon < 1986, 16 (Pt), 20 (Pd), 28 (Rh); sparrowhawk < 1986, 13 (Pt), 12 (Pd), 13 (Rh); gyrfalcon, 6 (Pt), 7 (Pd, Rh); grouse, 5 (Pt, Pd, Rh)

Table 4. Mean Pt, Pd, and Rh concentrations ± SE in flight feather shafts of sparrow and sparrowhawk (n is the number of samples)

	PGE (ng g^{-1})					
	Pt	n	Pd*	n	Rh	n
House sparrow	22.16 ± 11.06	6	7.02 ± 1.66	8	0.19 ± 0.13	7
Urban sparrowhawk	1.75 ± 0.81	21	2.12 ± 0.87	13	0.60 ± 0.17	18

* Indicative.

external contamination (Burger 1993), which is in agreement with our results showing a high background intensity level with several high, sharp peaks (Figure 5). The high background intensity is due to internally deposited metals, and the sharp peaks represent small externally attached particles. Background intensity is highest in sparrowhawks and peregrine falcon from south Sweden and lowest in gyrfalcon, grouse, and captive peregrine falcon. In house sparrows, the background Pb intensity is lower, but there are more sharp peaks than in sparrowhawks, reflecting increasing internal levels up the food chain and higher external exposure of sparrows.

PGE Relative Concentration Ratios. In Table 5, the Pt/Pd and Pt/Rh ratios in various urban environmental compartments and urban birds are summarized. Pt concentrations are approximately three to four times higher than Pd concentrations in road dust from high-traffic roads and airborne particles, PM 2.5 (Rauch 2001; Rauch *et al.* 2001a). In raptor feathers the Pt/Pd ratio is 0.3 to 1.1 with a mean of 0.7, suggesting a higher mobility of Pd and also indicating an internal contamination of Pd in addition to external contamination. The higher Pt/Pd ratio in sparrowhawks in relation to the other birds might be due to their hunting house sparrows, which are in direct contact with road dust and have a Pt/Pd ratio of 3.5 in their feathers. Higher concentrations of Pd than Pt and Rh have been measured in *Asellus aquaticus*, a freshwater macroinvertebrate, indicating a higher mobility of Pd, with bioavailability in the order Pd $\gg$ Rh $>$ Pt (Moldovan *et al.* 2001; Rauch 2001). A measurable transfer of PGE from contaminated soils to plants has been shown, with PGE transfer coefficients being in the range of

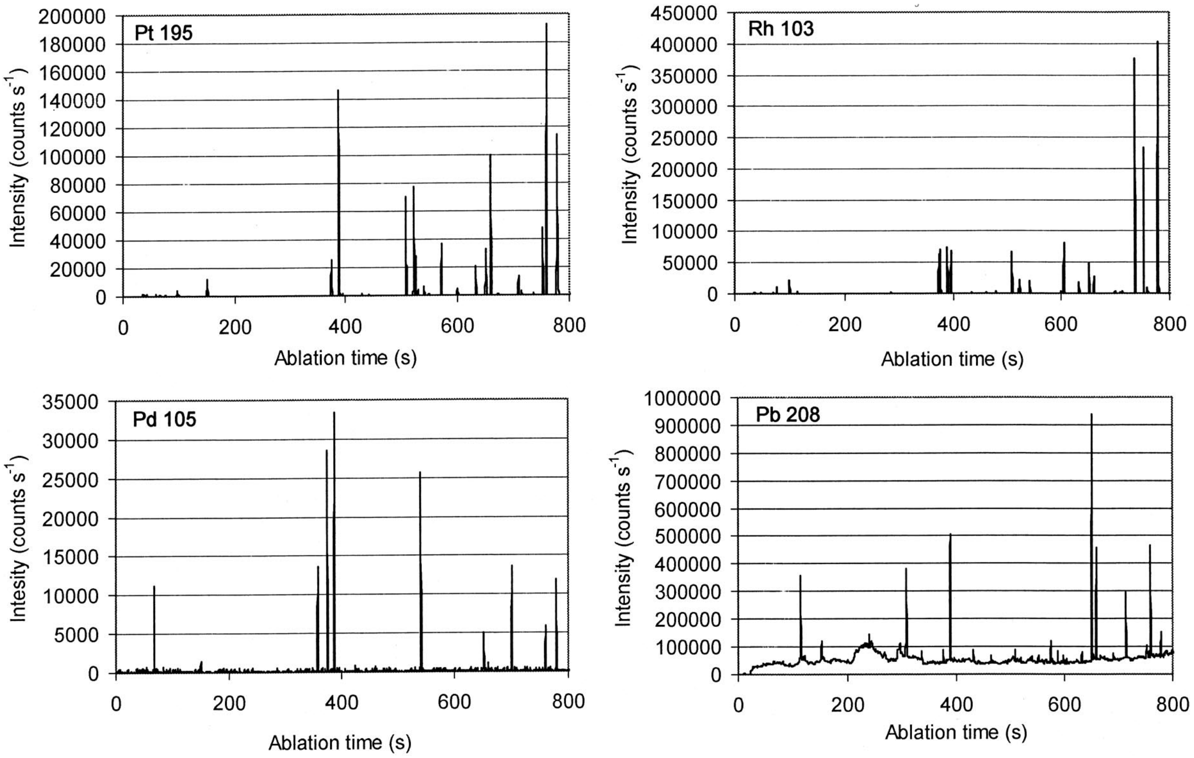

Fig. 5. Laser ablation scans of flight feather from a rural sparrowhawk for ^{195}Pt, ^{103}Rh, ^{105}Pd, and ^{208}Pb. Scan speed 50 μm s^{-1}, dwell time 1 ms

Table 5. PGE concentrations ± SD (SE for results from this study) and Pt/Pd and Pt/Rh ratios in different urban environmental compartments, sparrow, and urban sparrowhawk.

		PGE			Ratio		
	Unit	Pt	Pd	Rh	Pt/Pd	Pt/Rh	Reference
Natural crustal ratios	ng g^{-1}	0.4	0.4	0.06	1	6.7	Wedepohl (1995)
Road dust, high traffic	ng g^{-1}						Rauch (2001)
< 63 μm		341.3 ± 300.3	73.4 ± 66.2	112.5 ± 101.4	4.65	3.0	
63–250 μm		99.0 ± 52.6	30.2 ± 24.9	28.6 ± 15.8	3.3	3.5	
Airborne particles	pg m^{-3}						Rauch *et al.* (2001a)
PM10		14.1 ± 3.7	4.9 ± 3.1	2.9 ± 1.0	2.9	4.9	
PM2.5		5.4 ± 1.0	1.5 ± 0.5	1.6 ± 0.6	3.6	3.4	
House sparrow	ng g^{-1}	22.2 ± 11.06	7.0 ± 1.66	0.2 ± 0.13	3.5	4.2*	This study
Urban sparrowhawk	ng g^{-1}	1.75 ± 0.81	2.12 ± 0.87	0.60 ± 0.17	0.8	2.9	This study

* One observation.

immobile to moderately mobile elements, the same as Cu (Schäfer *et al.* 1998). The transfer coefficient decreased from Pd > Pt ≥ Rh; Pd therefore being the most biologically available of the PGEs. Up to 30% of the Pd present in road dust was shown to dissolve in an acid solution, and a solubility gradient of Pd > Rh > Pt was observed (Jarvis *et al.* 2001). However, Pd is difficult to measure due to interference during ICP-MS analysis (Rauch *et al.* 2001a), and the relative contribution of interferences to the total Pd concentration is high in the present study (Figure 1). Therefore, Pd levels are indicative.

The Pt/Rh ratio in feathers ranges from 0.7 to 2.9, with a mean ratio of 2, which is slightly lower than the Pt/Rh ratio of around 3.4 in road dust and airborne particles, PM 2.5 (Rauch 2001; Rauch *et al.* 2001a). Urban birds have a Pt/Rh ratio equal to that of road dust and airborne particles, indicating external contamination. It is suggested that Pt and Rh contamination of feathers is predominantly external. The ratios found in the present study indicate a bioavailability/mobility gradient from Pd > Rh ≥ Pt, as reported previously (Schäfer *et al.* 1998; Jarvis *et al.* 2001; Rauch 2001).

Conclusions

Evidence for an increasing temporal trend was observed in raptor feathers, reflecting the introduction of automobile catalyst exhaust systems. Rh concentrations were significantly higher in wild peregrine falcons from 1988–1999 compared to wild peregrine falcons from 1917–1982 as well as in sparrowhawk feathers from 1988–1996 compared to sparrowhawks from 1939–1986. No significant spatial trend could be established. However, Pt and Pd concentrations were significantly higher in house sparrows than in sparrowhawks in urban areas due to higher PGE exposure of house sparrows. No difference was found between a terrestrial and an aquatic food chain.

PGE contamination of feathers is predominantly external in the form of nanometer-sized particles externally attached to the feather. This is shown by the pattern obtained by laser ablation ICP-MS, where PGE occurs as randomly distributed peaks (*i.e.*, external particles) and by the significantly higher Pt and Pd concentrations in the vane compared to the shaft. The randomly distributed external particles are the proposed reason for relatively high standard errors for PGE concentrations. The association of PGE to Ce indicates that the origin of the particles is automobile catalysts.

Lower Pt/Pd ratios in feathers compared to other environmental compartments, such as road dust and airborne particles, suggests that Pd is more mobile in the environment. The raptor feather results demonstrate a bioavailability/mobility gradient of Pd $>$ Rh $\geq$ Pt, Pd contamination of feathers being both external and internal, and Pt and Rh contamination is predominantly external.

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