

The plant availability of auto-cast platinum group elements

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Abstract The introduction of automobile catalysts has raised environmental concern, as this pollution control technology is also an emission source for platinum group elements (PGE). The main aim of this study was to assess soil and grass PGE concentrations in soils adjacent to five road networks. The soil and grass samples were collected from four distances at each site; they were 0, 1, 2 and 5 m from the road edges. The maximum soil Pt, Rh and Pd concentrations were measured at the road perimeters. Pd concentrations were much higher than Pt or Rh, possibly due to differences in its use, emission and/or soil chemistry. Rh and Pt soil concentrations accounted for 66 and 34% ($P < 0.01$) of the variability observed, respectively, in their plant concentrations. Grass Pd concentrations had no relationship with its total soil concentrations.

Keywords PGE · Platinum · Palladium · Rhodium · Plant uptake

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Introduction

Automobile catalytic converters have been mandatory on new cars in the European Union since 1993. Most modern cars are fitted with a three-way catalytic converter that uses PGE, i.e. platinum (Pt), rhodium (Rh) and/or palladium (Pd) as catalysts for oxidation of hydrocarbons (HC) and reduction of nitrogen oxides (NO_x). The introduction of automobile catalytic converters has reduced the emissions of HC and NO_x from gasoline combustion by 90% (Barefoot 1997). However, there has been some concern that this pollution control technology is a source of PGE emissions, with potential to give rise to environmental contamination problems, since elevated PGE concentrations have been found in environmental and biological materials following their introduction in automobile catalytic converters (Ek et al. 2004).

PGE concentrations in road dust and adjacent soils generally decrease with distance from the road, indicating their deposition close to the source. Work on PGE deposition and accumulation in soils has largely focussed on road dust samples (e.g. Boch et al. 2002) and roadside soils gathered very close to road edges (e.g. Farago et al. 1998; Ely et al. 2001). The results of previous studies suggested that traffic emission-borne PGE are relatively inert, although this assessment was mainly based on studies of emitted metallic particles (Artelt et al. 1999). However, the detection of PGE in plants and trees adjacent to road networks (e.g. Djingova et al. 2003) suggests that

they may be undergoing post-depositional transformations in the soil into more environmentally reactive and bioavailable species. Results from hydroponic studies (e.g. Verstraete et al. 1998) provide clear evidence of PGE plant uptake, although the findings of such studies are not fully representative of their bioavailability under field conditions.

Here we report a study primarily designed to assess plant uptake of Pt, Pd and Rh from soils adjacent to several road networks in order to evaluate bioavailability within these localised environments.

Materials and methods

Five sites were chosen for this study, which included four locations around Oxfordshire and one site in outer west London. Site A was a flat verge on a main road (Oxford Ring Road, A40) leading up to a typical busy town roundabout, with traffic subject to regular stop/start patterns. Site B was on the intersection of a slip road with a main trunk road (Oxford Ring Road, A34) carrying heavy and quite steady traffic. Site C was on a road (A4074) that leads away from a busy town roundabout where vehicles would be actively accelerating. Site D was on a dual carriageway (A404) and approximately 400 m from an intersection, where traffic was normally freely moving. Site E was at the junction of the slip road with a busy dual carriageway (A40) carrying heavy and fairly fast-moving traffic.

The sampling was carried out on 13 July 2000 during a relatively dry spell of weather, although Spring 2000 had been much wetter than average in Oxford. The roadside soil and grass samples were collected from four distances at each site; these were 0, 1, 2 and 5 m from the road edge. For each sampling location grass and soil samples were collected from a 10-cm-wide and 5-m-long strip. We chose to sample cocksfoot grass (*Dactylis glomeratus*) as this was a distinctive species and represented at all five sites. The plant samples ($n = 10$) were clipped-off at approximately 2 cm above the ground and bagged as a composite for each sampling location and distance. Five soil cores from the top 2 cm were collected with a stainless steel trowel, which together formed a composite soil sample for each sampling location and distance.

The soil samples were air-dried, ground to $< 125 \mu\text{m}$, thoroughly homogenised and stored in sealed

polythene sample bags before analysis. For soil sample digestion, a procedure that involves the use of concentrated nitric acid (HNO_3) and hydrogen peroxide (H_2O_2) as in USEPA Method 3051a for soil digestion was used. The samples were digested in a standard batch format, using a microwave digestion system, and were subsequently filtered through Whatman No. 541 and diluted to 50 ml with ultra-pure water.

Individual composite plant samples were split into two equal sub-samples. In order to assess whether PGE concentrations in the grass samples are soil-borne or are derived from road-dust deposition on the plants, one of the sub-samples was first washed under running tap-water followed by thorough rinses in dilute acid, 0.01 M HCl (Analytical Grade) and ultra-pure water. Both washed and unwashed plant samples were oven dried at 60°C for 24 h before being finely ground in a PTFE centrifugal ball mill. Duplicate 0.5-g ground grass samples were digested in acid-washed PTFE pressure vessels with 5 ml HNO_3 (69%) and 1 ml 30% H_2O_2 , using a microwave digestion system. HNO_3 and H_2O_2 used in the soil and plant digestion techniques were of Aristar grade. All samples (soil and grass) were analysed by inductively coupled plasma mass spectrometry (ICP-MS). The detection limits for the method used are $0.105 \mu\text{g Pt kg}^{-1}$, $0.185 \mu\text{g Pd kg}^{-1}$ and $0.07 \mu\text{g Rh kg}^{-1}$. Although no certified reference materials (grass or soil) were included in the analysis, data integrity was maintained by implementing a number of quality-control protocols, including replicate analysis, with variability between replicates being generally $< 10\%$. For further quality control, a matrix-matched solution of known concentration was analysed several times during the analysis run. The % RSD figures for this analysis, while slightly variable across the elements, were $< 5\%$ ($n = 5$), and the average recovery was within $\pm 8\%$.

Results and discussion

The soil PGE contents differed between the sites regardless of the distance from the roads, as indicated by the relatively large standard deviation values (Table 1). The maximum soil Pt, Rh and Pd concentrations were measured at road perimeters; the concentrations decreased with distance away from

road perimeters. The average soil Pt concentration of $15.9 \pm 7.5 \mu\text{g kg}^{-1}$ at the 0-m distance (road perimeter) decreased to $2.04 \mu\text{g kg}^{-1}$ at the 5-m sampling distance away from the road (Table 1). Similarly the Rh concentration decreased from $22.4 \pm 4.7 \mu\text{g Rh kg}^{-1}$ at 0-m distance to $3.5 \pm 1.9 \mu\text{g Rh kg}^{-1}$ at 5-m distance. The Pt and Rh concentrations measured at 5-m distance are however greater than their background soil concentrations, which are considered to be similar to the earth's crust, i.e. $<1 \mu\text{g kg}^{-1}$ (Wedepohl 1995), whilst the results clearly show that Pt and Rh are deposited close to the source, i.e. traffic emissions, and the concentrations decline rapidly with distance away from the roads. The data also suggest that at least some of the Pt and Rh are transported beyond 5-m distance. This is consistent with previous findings that showed significant concentration of Pt in airborne coarse ($>2.5 \mu\text{m}$) and fine ($<2.5 \mu\text{m}$) particulate material at locations much further away from road networks (Schons 2004).

The Pd concentration also decreased with distance from roads; however its rate of decline was much slower compared to that of Pt and Rh. Furthermore, the Pd concentrations measured at all distances were much higher than Pt or Rh, the mean values ranging from $120.8 \pm 12.0 \mu\text{g Pd kg}^{-1}$ at the road perimeters to $84.2 \pm 10.9 \mu\text{g Pd kg}^{-1}$ at 5-m distance. The Pd concentrations are not surprising, as other studies

have reported similar or higher levels of Pd (e.g. Rauch and Hemond 2003). However, they represent a distinct distribution pattern in terms of the mean Pd concentration at 5-m distance ($84.2 \pm 10.9 \mu\text{g Pd kg}^{-1}$) that is many orders of magnitude greater than its background soil concentration (Wedepohl 1995). The greater concentrations of Pd compared to the other elements may either be due to the Pd particles being larger than those of Pt or Rh and/or to its greater emission than Pt and Rh, which showed broadly similar trends (Table 1). Furthermore, it should be noted here that local soil conditions (pH, organic matter, clay minerals, road salt application) can influence PGE post-depositional transformation (e.g. retention-release reactions), which, depending upon element-specific mobilisation or immobilisation processes, could offset expected PGE emission impacts.

The PGE plant concentrations, when pooled across all sampling locations and distances, show a considerable variability between and among individual metals, as evidenced by their mean and standard deviation values: $1.51 \pm 0.71 \mu\text{g Rh kg}^{-1}$, $9.42 \pm 4.96 \mu\text{g Pd kg}^{-1}$ and $8.25 \pm 6.74 \mu\text{g Pt kg}^{-1}$. The metal concentration data from washed and unwashed samples was compared using the t-test. The mean concentrations for washed and unwashed grass samples were 1.51 and $1.60 \mu\text{g Rh kg}^{-1}$, 9.42 and $10.04 \mu\text{g Pd kg}^{-1}$, and 8.25 and $8.94 \mu\text{g Pt kg}^{-1}$, respectively. However, no significant difference between washed and unwashed samples was found for any of the elements ($P > 0.05$). Nevertheless this demonstrates unequivocally that at least a fraction of the auto-cast PGE in soils adjacent to roads occurs in forms that are plant available. This also shows the significance of post-depositional processes and transformations in soils, which could mobilise auto-cast PGE into the wider environment, as their emission is thought to occur largely in the form of inert metallic oxide particles (Ek et al. 2004). Previous studies of PGE uptake by plants grown on soil from road verges (Schäfer et al. 1998), and their transfer to water bodies through stormwater and accumulation in sediments (Rauch and Hemond 2003), provide evidence of their environmental significance. Traces of these elements have also been detected in birds, fish and invertebrates, with obvious potential for their entry into the human food chain (Ek et al. 2004; Ravindra et al. 2003).

Table 1 Soil and grass PGE concentrations, mean \pm standard deviation ($\mu\text{g kg}^{-1}$ dry mass)

Distance from road (m)	Soil concentration	Grass concentration
<i>Platinum</i>		
0	15.94 ± 7.54	12.04 ± 8.26
1	9.18 ± 2.89	8.27 ± 6.92
2	4.13 ± 1.74	5.52 ± 3.15
5	2.04 ± 1.35	6.60 ± 6.69
<i>Rhodium</i>		
0	22.40 ± 4.73	2.34 ± 0.72
1	13.90 ± 6.22	1.31 ± 0.36
2	6.86 ± 3.54	1.51 ± 0.60
5	3.51 ± 1.96	0.90 ± 0.19
<i>Palladium</i>		
0	120.82 ± 12.03	14.28 ± 5.49
1	107.88 ± 10.67	7.48 ± 2.03
2	94.05 ± 8.94	7.98 ± 4.26
5	84.20 ± 10.88	7.13 ± 3.46

To assess the relationship between soil and grass PGE concentrations, the concentrations in (washed) grass samples were compared with their total soil concentrations. Rhodium soil concentration accounted for 66% ($P < 0.01$) of the variability observed in plant concentrations (Fig. 1). Similarly platinum plant concentrations were also significantly ($P < 0.01$) related to the soil concentrations, the relationship accounting for 34% of the variability in plant Pt concentrations (data not shown). Grass Pd had no relationship with its soil concentration, suggesting that most of the Pd at these sites may be in non-bioavailable forms. The bioavailability of metals is determined by soil metal concentrations together with soil type (e.g., pH, clay content and organic matter). Total soil metal concentration alone may not correlate with plant metal concentrations, particularly when different soils are compared, and is not considered a reliable test for assessing the risk of metal uptake by plants (Hooda et al. 1997). Clearly, further work is required to better understand PGE post-depositional transformations (e.g. solubility, adsorption, desorption) and to assess the influence of soil properties (e.g. pH, CEC, organic matter) on their bioavailability.

In conclusion, the work showed that maximum soil PGE concentrations were at road perimeters, which decreased with increasing distance away from roads. The Pt and Rh concentrations presented a similar distribution pattern in terms of their concentrations and decline with distance. The Pd soil concentrations were much higher than Pt and Rh, possibly reflecting the pattern of its emission. The Rh and Pt grass concentrations correlated with the soil concentrations, providing evidence of their uptake from the

soils and post-depositional transformations, since the emitted particles are generally considered to be inert. No such soil–plant relationship was found for Pd, suggesting that it may be in non-bioavailable forms or at least Pd bioavailability cannot be assessed by its total soil content at the study sites, a finding that merits further research on both particle size and distribution patterns and mechanisms of uptake.

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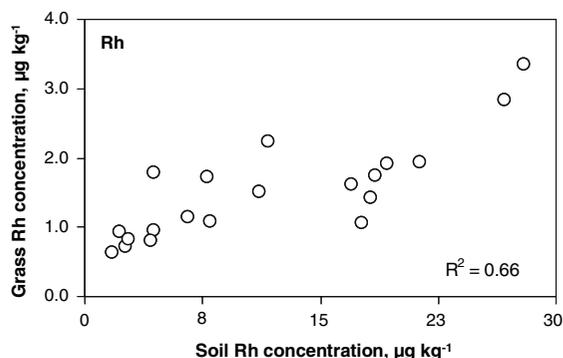


Fig. 1 Relationship between soil and grass Rh concentrations

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