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The estimation of the bioavailabilities of platinum, palladium and rhodium in vehicle exhaust catalysts and road dusts using a physiologically based extraction test

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ABSTRACT

Platinum group element (PGE) levels in the environment have increased following the introduction of vehicle exhaust catalysts (VECs). In order to evaluate the potential pathways of PGEs from VECs into humans, a physiologically based extraction test (PBET) was used to study the uptake of PGEs by the human digestive tract. The PBET assay was implemented in two phases, to first simulate the passage of ingested soil through the acid conditions of the stomach before it enters the near neutral conditions of the small intestine. The results showed that Pt, Pd and Rh did not undergo precipitation reaction when passing from the acid environment of the stomach to the neutral environment of the small intestine. The greatest fractions of bioavailable PGEs (up to 68%) were observed in road dust samples, possibly due to the presence of mobile PGE species formed in the roadside environment. Higher percentages of Pd and Rh were bioavailable than Pt, probably due to the differences in their mobilities and tendencies to form soluble complexes. Pt showed the highest absolute bioavailability however, due to its greater concentration in environmental samples. The solubilization of PGEs in the human digestive tract could involve the formation of PGE-chloride complexes, with perhaps increased health-hazard issues because of the known toxic and allergenic effects of these species.

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1. Introduction

The release of Pt, Pd and Rh from vehicle exhaust catalysts (VECs) represents a source of highly dispersed environmental contamination and these metals have been identified in a variety of dusts, soils and waters (Alt et al., 1993; Helmers, 1997; Zereini et al., 1997, 2001; Schafer, 1998; Hutchinson et al., 2000; Ely et al., 2000; Gomez et al., 2002, 2003). Emissions from VECs are thought to be mainly as fine particulate material from the abrasion and deterioration of the catalyst surface, with platinum group elements (PGEs) being deposited along roadways, on adjacent vegetation and soil, and dispersed in silt and water. Despite initial emissions are in metallic and oxide forms (Schlogl et al., 1987; Konig et al., 1992; Artelt et al., 2000), PGEs can interact with several different ligands in the

environment and be transformed into soluble species which can enter the food chain (Lustig et al., 1996, 1998a,b; Wood, 1996; Colombo et al., in press).

The toxicity of platinum, palladium and rhodium species has been investigated in various studies: in the metallic state, PGEs are non-toxic and non-allergenic, but some of their compounds, especially the chlorinated ones, are very toxic and allergenic (WHO, 1991, 2002). Indications of the acute toxicity of several PGE-chlorinated salts and evidence of DNA damage due to PGE exposure have been observed both *in vitro* and *in vivo* (WHO, 1991, 2002; Gagnon et al., 2006).

In order to investigate the uptake of PGEs in the human digestive tract, a physiologically based extraction test (PBET), which allows estimates of PGE bioavailability from soils and dusts, has been used in this study. Bioavailability generally

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refers to how much of a contaminant is “available” for uptake by humans or other organisms. Failure to gauge accurately the bioavailability of chemicals in the environment may lead to erroneous estimates of exposure for both human and ecological receptors. *In vivo* assessment of bioavailability using animal models can be difficult to interpret due to the physiological and lifespan dissimilarities between humans and the experimental species adopted. Moreover this approach is expensive and time consuming, and requires the use of animals. On the other hand, *in vitro* approaches are simple, cheap, fast and reproducible and are accepted by the US Environmental Protection Agency and the European Environment Agency.

When assessing risks from metal-contaminated soils and dusts, the exposure pathway usually evaluated is accidental soil ingestion by children for whom oral intake of soil contaminants may present a serious health risk. An epidemiological study demonstrated that the median soil intake by children ranged from 9 to 96 mg/day (Calabrese et al., 1989). Soil ingestion can also occur in adults for whom an average intake of 50 mg/day has been estimated (Calabrese et al., 1990). The Physiologically Based Extraction Test (PBET) (Ruby et al., 1996; Schoof, 2003) was therefore designed around pediatric gastrointestinal tract parameters for a child 2–3 years old. In the PBET assay, digestive juices based on human physiology are used to extract soil contaminants, in conditions that mimic those in the human digestive tract. The method is implemented in two phases, to first simulate the passage of ingested soil through the acid conditions of the stomach before it enters the near neutral conditions of the small intestine.

The PBET does not account for the presence of food in the gastrointestinal tract. Previous studies of interactions between metals and partially digested food in the stomach (Torre and Rodriguez, 1991) indicate that such material may adsorb metals, thereby reducing their net bioavailability. The PBET method may, therefore, be considered to represent a conservative scenario, yielding predicted metal absorption values which may exceed normal *in vivo* levels. Despite this limitation, the PBET is a well established procedure that has been used to quantify the bioavailability of arsenic and lead in soils and house dusts in the U.S.A. and U.K. (Ruby et al., 1996; Wragg and Cave, 2002).

In this study, the PBET was used to provide quantitative data on the bioavailability of PGEs in road dust, powdered exhaust catalyst and the metal hydroxides themselves.

2. Experimental procedure

2.1. Test materials

Two Certified Reference Materials (CRM) representative of (i) road dust with a maximum particle size of 90 μm , from the Institute of Reference Materials and Measurements, and (ii) powdered auto catalyst with a maximum particle size of 74 μm , from the National Institute of Standards and Technology (Table 1), were evaluated for PGE bioavailability in the PBET.

Road dust is a source of VEC-related contamination in the environment. The PGE concentrations in road dust have increased markedly during the past decades, reflecting traffic emissions (Ravindra et al., 2004). Road dust can be transported by wind as fine-grained particles and deposited on adjacent

Table 1 – PGE contents of certified reference materials employed in the PBET

Test material	Pt	Pd	Rh
Road dust CRM	81.3 $\mu\text{g/kg}$	6.0 $\mu\text{g/kg}$	12.8 $\mu\text{g/kg}$
Recycled catalyst CRM	1131 mg/kg	233.2 mg/kg	135.1 mg/kg

vegetation or in surface waters where dissolution can take place. Thus road dust can be transported and transformed into various parts of the environment where human beings, animals and plants can easily get exposed to it. Road dust was therefore employed in this study. Furthermore, a well characterized auto catalyst powder was used to represent the primary point of PGE dispersion.

Synthetic PGE-hydroxide species $\text{Pt}(\text{OH})_2$, $\text{Pd}(\text{OH})_2$ and $\text{Rh}(\text{OH})_3$ prepared from the appropriate nitrate complexes (Johnson-Matthey) by precipitation with NaOH, were also tested to provide a yardstick for the measurements. A synthetic “road dust” was made by mixing 4 parts by weight of each hydroxide with 88 parts of alumina powder.

1 g samples of road dust, catalyst and hydroxide/alumina mixture were used in the extraction tests.

2.2. PBET procedure

The PBET was carried out in sealed containers to minimize interactions between the reaction fluid and atmospheric oxygen and to eliminate possible cross contamination. The *in vitro* tests were each conducted in duplicate and a blank was also used.

A gastric solution for the PBET was prepared by adding 2.50 g of pepsin (activity of 800–2500 units/mg), 1.00 g of sodium citrate (Fisher Chemical Co), 1.00 g of malic acid (Aldrich Chemical Co), 840 μL of lactic acid (synthetic syrup 85% w/w) and 1 mL of acetic acid (Fisher Chemical Co) to deionized water (2 L). The pH of the solution was adjusted to 2.0 by adding concentrated HCl.

100 mL of gastric solution was combined with 1 g of test material in a reaction vessel (125 mL wide neck polyethylene bottle). The reaction vessels were half immersed in a temperature-controlled water-shaking bath heated to maintain a constant 37 °C in the reaction vessels. 5-mL stomach-phase samples were collected after 60 min using a syringe with a 2 μm filter. The solutions in the reaction vessels were then titrated to pH 7.0 with 1 M sodium bicarbonate (Fisher Chemical Co) solution and then 0.175 g of bile salts and 0.05 g of pancreatin were added to simulate conditions in the small intestine. Intestinal-phase samples were taken at 2 and 4 h after the reaction fluid reached equilibrium at pH 7. All samples were stored in a refrigerator at 4 °C until the analyses were performed.

2.3. PGE analysis

The concentrations of PGEs in solution in the PBET samples (both stomach and intestinal phase samples) were determined by inductively coupled plasma mass spectrometry (ICP-MS), using an ICP-MS Varian model 810. The operating conditions are given in Table 2.

ICP-MS is often used for the determination of PGEs in environmental samples (Barefoot, 1997; Bencs et al., 2003; Ek

Table 2 – ICP-MS operating conditions

Plasma	
Plasma flow:	18.00 L/min
Auxiliary flow:	1.80 L/min
Sheath gas flow:	0.20 L/min
Nebulizer flow:	1.00 L/min
Sampling depth:	5.50 mm
Power:	1.40 kW
Pump rate:	5 rpm
Stabilization delay:	10 s
Analysis Modes	
Analysis type:	Quantitative
Acquisition mode:	Steady state
Scan mode:	Peak hopping
Dwell time:	10,000 μ s
Replicates/sample:	3
Scans/replicates:	30
Analytes:	^{63}Cu , ^{65}Cu , ^{87}Rb , ^{87}Sr , ^{88}Sr , ^{89}Y , ^{103}Rh , ^{105}Pd , ^{179}Hf , ^{195}Pt , ^{206}Pb

et al., 2004; Ravindra et al., 2004) because of its excellent detection limits that allow accurate determination of PGEs in the ppt range. The determination of PGEs by ICP-MS is, however, hampered by spectral interferences from monatomic and polyatomic ions produced in the argon plasma by the matrix constituents: elements such as Cu, Y, Hf, Sr, Rb and Pb from road dust and catalyst samples cause interferences with the PGE signals (Table 3).

All the experimental solutions were prepared daily in 2% HNO_3 and matrix-matched using simulated gastrointestinal solutions identical to those employed in the PBET. PGE calibration standards were prepared by dilution of stock solutions of 1000 mg/L of Pt, Pd and Rh (in 20% HCl, all from Alfa Aesar, Johnson Matthey). The linearity of the calibration plots (correlation coefficient >0.99) was checked for Pt, Pd and Rh in the concentration range 0.1–100 $\mu\text{g/L}$. To compensate for instrumental drifts, 10 $\mu\text{g/L}$ of internal standards (ISs) were added to all samples. ^{115}In for ^{105}Pd and ^{103}Rh and ^{191}Ir for ^{195}Pt were selected as ISs because of their low abundance in the sample matrix and their similar atomic masses and chemical and physical properties to the PGEs. For the interference studies, single element stock solutions (1000 mg/L) of Cu, Rb, Sr, Y, Hf and Pb were used (all from Alfa Aesar, Johnson Matthey).

3. Results and discussion

3.1. Interference correction

The isotopes ^{195}Pt , ^{105}Pd and ^{104}Rh were used to determine the concentrations of Pt, Pd and Rh, respectively, in the samples because of their high natural abundances and because they are subject to fewer interferences; possible interferences are reported in Table 3.

Interferences were corrected mathematically by estimating the contribution of interfering species to the PGE signal through the analysis of single element standard solutions of interferents (Moldovan et al., 1999; Gomez et al., 2000; Rauch et al., 2001). The concentrations of the interfering elements in

the standard solutions were at similar levels to those in the sample solutions. Corrections were calculated using the following equation:

$$S_A = S_{A,S} - (S_{I,S}R_{IO})$$

where S_A is the corrected analyte (A) signal, $S_{A,S}$ is the interfered analyte signal measured for the sample solution, $S_{I,S}$ is the signal for the interfering element (I) in the sample solution, and R_{IO} is the signal ratio IO^+/I^+ (ratio between the concentration of the ions produced in the plasma that interfere on the PGE signal and the concentration of the interfering element itself, i.e. $^{40}\text{Ar}^{63}\text{Cu}^+/\text{Cu}^+$). The signal ratio R_{IO} for all the interfering species needed in the correction equations were measured daily. This mathematical correction method requires a linear dependence of the IO^+ signal on the I^+ concentration. In this study, a linear dependence was observed for all the interfering elements.

Considering all the interferences, the corrections for Pt, Pd and Rh were:

$$\begin{aligned} S_{\text{Pt}} &= S_{\text{Pt},S} - (S_{\text{Hf},S}R_{\text{HfO}}) \\ S_{\text{Pd}} &= S_{\text{Pd},S} - (S_{\text{Cu},S}R_{\text{ArCu}} + S_{\text{Y},S}R_{\text{YO}} + S_{\text{Sr},S}R_{\text{SrO}} + S_{\text{Rb},S}R_{\text{RbO}}) \\ S_{\text{Rh}} &= S_{\text{Rh},S} - (S_{\text{Cu},S}R_{\text{ArCu}} + S_{\text{Sr},S}R_{\text{SrO}} + S_{\text{Rb},S}R_{\text{RbO}} + S_{\text{Pb},S}R_{\text{Pb}}) \end{aligned}$$

Unfortunately, the determination of Pd in road dust was hampered by the extremely low Pd concentrations in the samples and the high content of interfering elements in the matrix.

3.2. PBET results for PGEs

The duplicate PBET tests gave reproducible results and the blank sample analysis showed that the gastrointestinal solution did not interfere with the PGE signal (Table 4).

Comparison of the PBET results for the three different test materials (road dust, milled catalyst and hydroxide/alumina mix) showed that bioavailability changes with substrates with the road dust samples showing much higher percentages of bioavailable PGEs than either the catalyst or the hydroxide samples. The road dust samples showed bioavailable Pt=15.7–16.7% and bioavailable Rh=63.6–67.5%, whereas for the catalyst and hydroxide samples, the percentage of bioavailable PGEs was less than 1% and 3%, respectively. These results support previous suggestions that PGEs in road dust are transformed from a metallic form to much more soluble species, probably through complexation by inorganic ions (Colombo et al., in press) and/or humic substances commonly found in the environment (Lustig et al., 1996, 1998a,b; Wood, 1996).

The PBET results for the road dust samples show that PGE dissolution is not strongly pH dependent: the stomach (acid) and intestinal (neutral) phases of the extraction tests gave closely similar bioavailability values. This indicates that there were no precipitation reactions involving PGEs at neutral pH conditions, since the PGEs stayed in solution even after an increase in pH (from pH=2 for the stomach phase to pH=7 for

Table 3 – Possible interferences in the ICP-MS determination of ^{195}Pt , ^{105}Pd and ^{103}Rh (Gomez et al., 2000)

Analyte	Possible interfering species			
^{195}Pt	$^{179}\text{Hf}^{16}\text{O}^+$			
^{105}Pd	$^{40}\text{Ar}^{65}\text{Cu}^+$	$^{89}\text{Y}^{16}\text{O}^+$	$^{88}\text{Sr}^{17}\text{O}^+$	$^{87}\text{Rb}^{18}\text{O}^+$
^{103}Rh	$^{40}\text{Ar}^{63}\text{Cu}^+$	$^{87}\text{Sr}^{16}\text{O}^+$	$^{87}\text{Rb}^{16}\text{O}^+$	$^{206}\text{Pb}^{2+}$

Table 4 – PBET results for PGEs

Sample	Platinum	
	Absolute bioavailability (ppb)	% bioavailable
Blank		
S	n.d.	–
I1	n.d.	–
I2	n.d.	–
Road dust		
S	0.125–0.129	15.5–16.0
I1	0.132–0.134	16.3–16.5
I2	0.138–0.133	17.0–16.4
Catalyst		
S	14.3–14.1	0.1
I1	37.8–36.7	0.3
I2	36.4–38.2	0.3
Hydroxide		
S	17.6–18.6	0.01
I1	29.2–30.8	0.01
I2	32.7–32.6	0.01
Sample	Palladium	
	Absolute bioavailability (ppb)	% bioavailable
Blank		
S	n.d.	–
I1	n.d.	–
I2	n.d.	–
Road dust		
S	—	–
I1	—	–
I2	—	–
Catalyst		
S	6.39–6.20	0.3
I1	19.2–19.6	0.8–0.9
I2	20.1–20.9	0.9
Hydroxide		
S	4872–4898	1.7
I1	7733–7730	2.7
I2	7800–7794	2.7
Sample	Rhodium	
	Absolute bioavailability (ppb)	% bioavailable
Blank		
S	n.d.	–
I1	n.d.	–
I2	n.d.	–
Road dust		
S	0.0829–0.0836	64.8–65.6
I1	0.0868–0.0863	68.0–67.2
I2	0.0801–0.0822	62.5–64.1
Catalyst		
S	8.10–7.77	0.6
I1	9.76–9.94	0.7
I2	9.87–9.94	0.7
Hydroxide		
S	53.2–53.1	0.02
I1	86.8–86.6	0.04
I2	96.0–97.1	0.04

S: stomach phase sample, I1: first intestinal phase sample and I2: second intestinal phase sample. (n.d.: not detected, —: determination not possible due to interferences). The bioavailability ranges reported corresponds to the results of the PBET duplicates.

the intestinal phases). For the catalyst and hydroxide samples, the PGE bioavailabilities slightly increased from stomach to intestinal phases, probably because of the longer residence times in the latter. For all the substrates analysed, the dissolved Pt, Pd and Rh in the small intestine phase remained generally constant as the residence time increased.

For the catalyst and hydroxide samples, the percentages of bioavailable PGEs were in the following order: Pd>Rh>Pt, consistent with several solubility studies (Ek et al., 2004; Ravindra et al., 2004). The PBET results also showed that, for road dust samples, more Rh was dissolved than Pt. The different bioavailability of Rh and Pt in environmental samples (i.e. road dust) can be attributed to the different transformations of the two VEC-emitted metals once deposited in the environment. This assumption is in agreement with the more mobile nature of Rh (Rauch et al., 2000) and its higher tendency to form complexes with humic substances than Pt (Wood, 1996). The Pd bioavailability in road dust samples (which could not be determined because of the interference issue, see Section 3.1) would probably be the greatest due to the highly soluble and mobile nature of this element (Ek et al., 2004; Ravindra et al., 2004).

The PBET results for the absolute PGE bioavailabilities showed however that for road dust samples the amount of bioavailable Pt was greater than the amount of bioavailable Rh and for the catalyst samples, the absolute bioavailability order was Pt>Pd>Rh (Table 3). These results reflected the relative PGE concentrations in the environmental samples (i.e. road dust and catalyst) employed in the PBET (Table 1). It can therefore be concluded that, despite Pd and Rh being more soluble and mobile than Pt (% bioavailability is in the order Pd>Rh>Pt), the higher amount of Pt present in the samples accounts for its highest absolute bioavailability in the gastrointestinal tract.

From the mid 1990s, a new trend has however been observed in VEC design, namely an increase in the amount of Pd. Although Pt is an efficient oxidation catalyst, it is more expensive and sensitive to poisoning than Pd. In the future, it is very likely that Pd-based VECs will become more widely used than Pt-based units. Pd could therefore become the most prevalent PGE emitted into the environment by VECs. This trend will need particular attention because of the more soluble and mobile nature of this element and its higher uptake by animals (Ek et al., 2004).

From the toxicological perspective, it is important to consider the possible formation of PGE-chloride complexes in the stomach environment due to the presence of HCl. It has been shown that, in acidic conditions and in the presence of chloride ions, PGE-chloride species can be formed (Fuchs and Rose, 1974; Colombo et al., in press), perhaps with increased health risks because of the toxicity of these compounds. Indeed, acute toxicity of PGE-chloride salts in laboratory mammals, including death, cardiovascular effects, reproductive toxicity and DNA mutagenicity, have been observed, as well as powerful allergenic effects on human beings (WHO, 1991, 2002). Besides, histological and pathological analysis of Sprague–Dawley rats (Gagnon et al., 2006) fed with a mixture of H₂PtCl₆, PdCl₂ and RhCl₃ (concentration ranging from 0.1 ppm to 10 ppm) revealed vacuolization, eosinophil inclusion bodies in adrenal glands, shrinkage of glomeruli in the kidney, enlargement of white pulp in the spleen and DNA damage even at the lowest PGE concentration.

4. Conclusion

The data presented in this study demonstrate the value of the *in vitro* PBET for determining the bioavailability of PGEs in environmental samples. The method is cost effective, fast, simple and adaptable to the analysis of a large number of samples.

The PBET results reported here for the different test materials (road dust, catalyst and hydroxide/alumina mixtures) confirm the importance of metal speciation when assessing bioavailability. PGEs in road dust samples are likely to have been transformed into soluble and mobile species through complexation by organic and inorganic ligands common in the roadside environment, therefore providing greater fractions of bioavailable PGEs than the unaltered hydroxide and catalyst samples. The elevated dissolution (up to 68%) observed for PGEs from road dust indicates that the PGE post-ingestion bioavailabilities are of the same order of magnitude as their total concentrations. This information needs particular attention in view of the ever-increasing levels of PGEs in the environment due to VEC emissions.

The negligible pH dependence observed for the PGE bioavailabilities indicate that Pt, Pd and Rh do not undergo precipitation reactions when passing from the acid environment of the stomach to the neutral environment of the small intestine.

The PBET results also support the assertion that Pd and Rh have higher mobilities and biological uptakes compared with Pt: the % bioavailability follows the order Pd > Rh > Pt. The different % bioavailabilities of Pt, Pd and Rh are attributed to the differences in their tendencies to form soluble complexes and to the different transformations of the metals in the environment. The highest absolute bioavailability is observed for Pt, however, because of its greater concentration in the road dust and catalyst samples.

An important consideration to bear in mind is that the solubilization of Pt, Pd and Rh in the human digestive tract could be in part due to, or involve, the formation of PGE-chloride complexes, which raises health-hazard issues because of the known toxic and allergenic effects of these species on animals and human beings.

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