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Environmental risk of particulate and soluble platinum group elements released from gasoline and diesel engine catalytic converters

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Abstract

A comparison of platinum-group element (PGE) emission between gasoline and diesel engine catalytic converters is reported within this work. Whole raw exhaust fumes from four catalysts of three different types were examined during their useful lifetime, from fresh to 80 000 km. Two were gasoline engine catalysts (Pt–Pd–Rh and Pd–Rh), while the other two were diesel engine catalysts (Pt). Samples were collected following the 91441 EUDC driving cycle for light-duty vehicle testing, and the sample collection device used allowed differentiation between the particulate and soluble fractions, the latter being the most relevant from an environmental point of view. Analyses were performed by inductively coupled plasma-mass spectrometry (ICP-MS) (quadrupole and high resolution), and special attention was paid to the control of spectral interference, especially in the case of Pd and Rh. The results obtained show that, for fresh catalysts, the release of particulate PGE through car exhaust fumes does not follow any particular trend, with a wide range (one–two orders of magnitude) for the content of noble metals emitted. The samples collected from 30 000–80 000 km present a more homogeneous PGE release for all catalysts studied. A decrease of approximately one order of magnitude is observed with respect to the release from fresh catalysts, except in the case of the diesel engine catalyst, for which PGE emission continued to be higher than in the case of gasoline engines. The fraction of soluble PGE was found to represent less than 10% of the total amount released from fresh

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catalysts. For aged catalysts, the figures are significantly higher, especially for Pd and Rh. Particulate PGE can be considered as virtually biologically inert, while soluble PGE forms can represent an environmental risk due to their bioavailability, which leads them to accumulate in the environment.

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1. Introduction

Spark-ignition (gasoline) and compression-ignition (diesel) engines are a major source of urban air pollution. Carbon monoxide (CO), unburned or partially burnt hydrocarbons (HC) and nitrogen oxides (NO_x) are the main contaminants present in engine exhaust fumes. Due to increasing ecological awareness of the need for the preservation of acceptable environmental conditions, catalytic exhaust after-treatment technologies for gasoline- and diesel-powered vehicles have been developed. These technologies were classified according to engine type, which determines the catalyst operating conditions.

The gasoline engine, which is the most popular today, is supported by the use of three-way catalysts (TWC). This oxidises CO and HC to CO_2 and H_2O, while at the same time reducing NO_x to N_2. Pt and Pd are involved in the oxidation of HC and CO, while Rh is used in the reduction of NO_x. The diesel engine, which is the second most popular, is supported by the use of oxidation catalysts, which were put on the market in 1991 for diesel passenger cars. A diesel oxidation catalyst converts a large part of the hydrocarbon constituents of the soluble organic fraction, as well as gaseous HC, CO and odour-creating compounds to CO_2 and H_2O. In a typical diesel oxidation catalyst, Pt or Pd is used (Lox and Legler, 1999).

A three-way catalyst consists of a catalytic unit contained in a stainless steel housing. The three principal parts of the catalytic unit are: (i) the substrate, typically a cordierite honeycomb monolith; (ii) the washcoat, a highly porous alumina coating on the substrate, which provides a high surface area for the catalytic reactions; and (iii) the catalyst material, some combination of platinum, palladium and/or rhodium. A key factor affecting the performance of the catalyst system is the type, quantity and distribution of the platinum group elements (PGE) on the washcoat layer (Mooney, 1996). In a similar manner, the diesel oxidation catalyst consists of a ceramic monolith on which a special washcoat is deposited, which contains the precious metal components.

Since the introduction of catalytic converters in the United States in the 1970s and in Europe in the 1980s, there has been a clear link between their use and the increasing concentration of PGE in the environment. Under real driving conditions, thermal and chemical mechanisms led to a partial release of PGE into the environment through car exhaust fumes (Stenbom, 1994).

Although other sources of PGE are possible in highly populated cities, none of them can be established as comparable in importance to catalyst contamination. Previous research has tended to focus on the release of particulate Pt from gasoline engine catalysts (Hill and Mayer, 1977; Rosner and Hertel, 1986; König et al., 1992; Knobloch et al., 1994; Artlet et al., 2000) and very little is known about the release of Pd and Rh (Lüdke and Hoffmann, 1996; Moon and Donald, 1998). Until now, no data on PGE emissions from diesel engine catalysts have been published.

It is believed that PGE are emitted from catalytic converters in particulate form, mainly in the (0) oxidation state or as oxides. Nanocrystalline PGE particles are attached to aluminium oxide, and the largest fraction comprises PGE-loaded particles with sizes >10 μm. From a toxicological point of view, soluble PGE species are more bioavailable and have the potential to directly affect organisms and plants, and therefore they present a greater environmental risk. To date, very little research has been carried out in this field. According to König et al. (1992), approximately 10% of the total platinum emissions are water-soluble. In

Table 1
Catalyst specifications

Catalyst type	Noble metals loading	Car/engine[a]
Catalyst A gasoline (Pt/Pd/Rh)	Front brick Pt/Rh ratio 5:1; rear brick Pd/Rh ratio 9:1	Ford Fiesta van 1.3 l
Catalyst B gasoline (Pd/Rh)	Single brick Pd/Rh ratio 9:1	Ford Fiesta van 1.1 l
Catalyst C_1 diesel (Pt)	Single brick Pt (1.29 g per catalyst)	Seat Ibiza 1.9 l
Catalyst C_2 diesel (Pt)	Single brick Pt (1.29 g per catalyst)	Seat Ibiza 1.9 l

[a] Engine refers to the automobile engine to which the catalyst was connected for ageing and sampling.

engine test-bench studies by Artlet et al. (2000), the soluble fraction was approximately 1%.

In this work, a systematic study has been carried out under controlled laboratory conditions, in order to monitor the release of particulate and soluble Pt, Pd and/or Rh from two gasoline and two diesel engine catalysts throughout their useful lifetime.

2. Experimental

Two car manufacturers (Ford, Madrid, Spain; and Seat, Barcelona, Spain), a research institute (INTA, Madrid, Spain), and five European analytical laboratories (UCM, Madrid, Spain; Chalmers, Gothenburg, Sweden; USFD, Sheffield, United Kingdom; ISS, Rome, Italy; and GSF, Neuherberg, Germany) participated in this investigation.

2.1. Catalytic converters

The catalytic converters studied were representative of gasoline and diesel catalysts manufactured in 1998. The cars into which each catalyst was installed were also representative of the European car pool. Table 1 shows the main characteristics of each catalyst, together with the type of car/engine into which each one was installed. Two gasoline catalysts (A and B) and two diesel catalysts (C_1 and C_2) were used for this study. Although not labelled in catalyst B specification, a pre-catalyst was placed in the front part of the system. The specifications provided by the suppliers gave no information about other metal oxides, namely CeO_2, La_2O_3, ZrO_2, BaO, TiO_2, Y_2O_3 and NiO, content in the washcoat of the catalysts studied. The two gasoline catalyst-equipped cars were supplied by Ford, and the two diesel catalyst-equipped cars were supplied by Seat.

2.2. Ageing

Each catalyst was aged from fresh to 80 000 km through a vehicle ageing cycle. This condition enabled us to investigate and compare the behaviour of each catalyst along its life cycle, thus avoiding the uncertainty produced by different age-based behaviours in the different catalysts. After every 10 000 km, each car was checked in order to ensure good car/engine performance.

After carefully considering the different possibilities of ageing under controlled conditions, a representative one was chosen as follows: the catalysts were aged in a roller-controlled dynamometer following a driving cycle, which represented urban and non-urban driving conditions. The ageing cycle consisted of 1 h constant speed periods running at 80, 65, 90, 70 and 115 km h^{-1}, followed by a 0.5 h period running at 84 km h^{-1}. The whole ageing cycle lasted 5.5 h. The gasoline catalysts were aged at the INTA laboratories and the diesel catalysts were aged at the Seat laboratories.

2.3. Sampling strategy

Samples were taken directly from the car exhaust pipe using a homemade device already described (Moldovan et al., 1999). This device was designed to bubble all raw exhaust fumes through two containers containing an absorbent solution capable of retaining the soluble and particulate PGE released by the catalyst. The exit speed of the exhaust fumes was high enough to prevent particle retention in the connecting tubes or in the bubblers, and no cracks in the bubblers or obstruction of their holes were observed. The device used was robust and resistant to high temperature and pressure; no backpressure effect was observed.

Samples were taken following the 91441 EUDC driving cycle for light-duty vehicle testing. This is a combination of four urban (ECE) cycles and one non-urban (EUDC) cycle through a series of accelerations, decelerations and steady speeds. Each urban cycle covered a distance of 1.013 km during 195 s at a mean speed of 19 km h^{-1}, reaching a maximum speed of 50 km h^{-1}. The non-urban cycle covered a distance of 6.955 km during 400 s at a mean speed of 62.6 km h^{-1}, reaching a maximum speed of 120 km h^{-1}. The whole driving cycle lasted approximately 20 min over a distance of 11.007 km. The driving cycle did not include acceleration episodes at high speed.

For each catalyst, four sampling campaigns were carried out: fresh (0 km), 30 000, 60 000 and 80 000 km. The sampling was performed by UCM at the INTA laboratories for the gasoline catalysts and at the Seat laboratories for the diesel catalysts.

2.4. Sample preparation and analysis

Within 15 min from sampling, the total sample volume (approx. 2 l) was filtered through a cellulose ester filter of 47 mm in diameter and 0.45 μm pore size. The filtered solutions contained the soluble PGE fraction, while the particulate fraction was retained on the filter. PGE contained in the filtered solution were stabilised in HCl 2% (v/v) at the sampling place. Particulate PGE retained on the filter were mineralised mainly using acid-assisted high-pressure ashing (HPA) and acid-assisted microwave (MW) irradiation. *Aqua regia*/HF or *aqua regia*/$HClO_4$, with and without UV oxidation, were the reagents used for total mineralisation of the filters. The soluble PGE were analysed without previous treatment. All the reagents used were of Suprapur grade.

Analyses of soluble and particulate fractions were performed by quadrupole (Q) ICP-MS (PQ3 VG Elemental; HP 4500 Hewlett Packard; ELAN 6000 Perkin Elmer) and high-resolution (HR) ICP-MS (Element, Finnigan MAT). Special attention was paid to interference control, especially for Pd and Rh determination.

A total of 1280 samples were analysed [four catalysts, four sampling campaigns per catalyst, four samples per analytical laboratory, four subsamples per sample (two particulate and two soluble fractions), and five analytical laboratories] during the whole study.

2.5. Quality assurance

The determination of PGE by ICP-MS, especially at very low concentration levels, presents serious analytical difficulties, and therefore it is important to assess the quality of the results obtained.

The analytical laboratories carried out internal quality control (QC) by analysing the samples by two different techniques (DP-CSV and ICP-MS for Pt and Rh) or analysing two specimens of used autocatalyst powder certified reference materials (CRM), such as NIST 2557 and IMEP-11. Standard PGE solutions and solutions of mineralised gasoline and diesel filters stabilised in two different acid media, 10% HCl (v/v) and 10% *aqua regia* (v/v), were prepared as external QC, and sent to the analytical laboratories within each sampling dispatch. In all cases, the results obtained by the analytical laboratories were in good agreement.

3. Results

Concern about a high increase in PGE concentrations in traffic-exposed samples led to an international co-operation under the CEPLACA project (Palacios, 1997) funded by the European Union. The CEPLACA project dealt with the assessment of the environmental contamination risk by Pt, Rh and Pd from automobile catalysts. One main objective was the study of representative diesel and gasoline catalyst behaviour from their fresh to spent conditions by measuring the amount of soluble and particulate forms of PGE released along their useful life.

In a previous work (Palacios et al., 2000), it was shown that exhaust fume samples collected from fresh catalytic converters exhibit non-homo-

Table 2
PGE in exhaust fumes collected from a gasoline car fitted with a Pt–Pd–Rh catalyst (A)

	PGE (ng km^{-1})		
	Platinum	Palladium	Rhodium
0 km			
Particulate			
Range	33.2–313.4	22.0–108.0	10.3–253.0
Arithmetic mean	111.5	54.2	76.9
10th–90th percentiles	38.1–183.9	24.5–100.7	17.3–215.8
Class mean (0.2)	111.5	54.2	76.9
Median	106.1	37.5	25.9
Soluble			
Range	ND–5.7	2.0–14.1	0.3–5.0
Arithmetic mean	1.6	8.7	2.6
20th–80th percentiles	0.2–2.5	5.8–11.5	1.0–3.9
Class mean (0.4)	0.9	8.9	2.8
Median	0.6	9.5	3.4
30 000–80 000 km			
Particulate			
Range	2.0–22.1	1.4–19.0	0.6–11.1
Arithmetic mean	8.8	7.9	2.8
10th–90th percentiles	3.9–15.2	2.4–15.3	1.0–5.2
Class mean (0.2)	8.3	7.6	2.5
Median	7.5	6.3	2.4
Soluble			
Range	ND–1.8	ND–44.2	ND–15.9
Arithmetic mean	0.5	10.6	3.4
20th–80th percentiles	ND–0.8	2.2–15.6	ND–7.3
Class mean (0.4)	0.4	7.5	2.2
Median	0.2	7.1	1.7

geneous PGE release behaviour compared to those collected at 30 000 km. Catalytic converter manufacturers consider the first 6400 km in the life of the catalyst as a break-in portion, and therefore they are not representative of the normal catalytic converter behaviour (Mooney, 1996). Therefore, for a better discussion, the data obtained during the whole study were subdivided into two groups: 0 and 30 000–80 000 km.

The particulate and soluble PGE emission data of all samples analysed are summarised in Tables 2–5. Owing to the particular inhomogeneous release of PGE from the catalyst surface, the usual criteria for discarding data could not be applied. Therefore, although several statistical parameters are shown in the tables, the discussion will be based on the values obtained for the percentiles (10th–90th for the particulate fraction and 20th–80th for the soluble fraction), class mean (0.2 for the particulate fraction and 0.4 for the soluble fraction), and median for both particulate and soluble fractions.

3.1. Particulate PGE emissions

For the fresh catalysts the particulate release (class mean) was: 111.5 ng km^{-1} of Pt, 54.2 ng km^{-1} of Pd, and 76.9 ng km^{-1} of Rh for the Pt–Pd–Rh gasoline catalyst; 43.2, 41.6 and 11.7 ng km^{-1} of Pt, Pd and Rh, respectively for the Pd–Rh gasoline catalyst; and a medium value of 82.2 ng km^{-1} of Pt for both diesel catalysts. After ageing (30 000–80 000 km), the particulate release (class mean) was: 8.3 ng km^{-1} of Pt, 7.6 ng km^{-1} of Pd, and 2.5 ng km^{-1} of Rh for the Pt–Pd–Rh gasoline catalyst; 5.4, 7.2 and 2.2 ng km^{-1} of Pt, Pd and Rh, respectively for the Pd–

Table 3
PGE in exhaust fumes collected from a gasoline car fitted with a Pd–Rh catalyst (B)

	PGE (ng km^{-1})		
	Platinum	Palladium	Rhodium
0 km			
Particulate			
Range	15.7–128.3	15.5–132.1	4.4–33.0
Arithmetic mean	43.2	41.6	11.7
10th–90th percentiles	18.9–82.4	17.0–85.1	5.5–21.5
Class mean (0.2)	43.2	41.6	11.7
Median	28.3	22.6	8.3
Soluble			
Range	ND–5.1	0.9–4.5	ND–4.2
Arithmetic mean	2.0	3.8	1.4
20th–80th percentiles	1.7–2.0	2.5–4.8	0.2–2.0
Class mean (0.4)	1.9	3.6	1.1
Median	1.9	3.6	1.3
30 000–80 000 km			
Particulate			
Range	1.1–16.8	1.9–21.5	0.3–24.1
Arithmetic mean	5.7	7.7	3.2
10th–90th percentiles	2.7–8.6	3.6–13.2	1.0–3.9
Class mean (0.2)	5.4	7.2	2.2
Median	5.4	6.3	2.1
Soluble			
Range	ND–33.9	0.2–47.7	ND–28.6
Arithmetic mean	1.1	12.7	5.6
20th–80th percentiles	ND–0.7	3.5–21.6	ND–8.1
Class mean (0.4)	0.4	9.8	15.9
Median	0.3	8.8	2.2

Rh gasoline catalyst; and a medium value of 128.6 ng km^{-1} of Pt for both diesel catalysts.

3.2. Soluble PGE emissions

For fresh catalysts the soluble release (class mean) was: 0.9 ng km^{-1} of Pt, 8.9 ng km^{-1} of Pd, and 2.8 ng km^{-1} of Rh for the Pt–Pd–Rh gasoline catalyst; 1.9, 3.6 and 1.1 ng km^{-1} of Pt, Pd and Rh, respectively for the Pd–Rh gasoline catalyst; and a mean value of 1.8 ng km^{-1} of Pt for both diesel catalysts. After ageing (30 000–80 000 km), the particulate release (class mean) was: 0.4 ng km^{-1} of Pt, 7.5 ng km^{-1} of Pd, and 2.2 ng km^{-1} of Rh for the Pt–Pd–Rh gasoline catalyst; 0.4, 9.8 and 15.9 ng km^{-1} of Pt, Pd and Rh, respectively for the Pd–Rh gasoline catalyst; and a mean value of 5.0 ng km^{-1} of Pt for both diesel catalysts.

4. Discussion

From 30 000 to 80 000 km of operation, both gasoline catalysts show a particulate PGE release that, in the worst case, only differs by approximately one order of magnitude from sample to sample, this being observed for all three elements. Although the two gasoline catalysts studied belong to different types, they represent similar behaviour with respect to PGE release. The results obtained during the whole test period indicate good performance of both gasoline catalysts, with low deactivation due to surface abrasion and subsequent loss.

Artlet et al. (2000) studied the particulate Pt emission factor from three-way catalytic converters. The data (arithmetic mean) from fresh (12–90 ng km^{-1}) and aged catalytic converters (9–26 ng km^{-1}) installed on a medium-powered gasoline engine (1.8 l) showed a tendency towards decreasing platinum emission with increasing age. These results are in good agreement with our Pt emission factor (arithmetic mean) of 111.5 ng km^{-1} for the fresh and 8.8 ng km^{-1} for the aged catalyst A (Pt–Pd–Rh gasoline engine). No comparison can be made with particulate Pd and Rh released, because these determinations were not addressed in the work by Artlet et al. (2000).

Diesel catalysts labelled as ‘Pt-only’ show a less uniform behaviour in the 30 000–80 000-km range. Particulate PGE release also differs by approximately one–two orders of magnitude between samples, and the Pt content in exhaust fumes is approximately two orders of magnitude higher when compared with the gasoline catalyst exhaust. The differences in washcoat composition and diesel engine running conditions are probably the reason for this change in behaviour.

Gasoline catalysts release PGE in the low ng km^{-1} level throughout their lifetime, whereas diesel catalysts release 10–100-fold more Pt compared to the gasoline ones. However, most of the PGE content is retained by the converters after extended use. It must be pointed out that the data presented in this work correspond to exhaust fume samples collected under controlled conditions from cars having good performance. Real driving conditions are subject to factors such as engine mal-

Table 4
PGE in exhaust fumes collected from a diesel car fitted with a Pt catalyst (C_1)

	PGE (ng km^{-1})		
	Platinum	Palladium	Rhodium
0 km			
Particulate			
Range	30.8–406.6	4.2–84.4	6.6–75.4
Arithmetic mean	133.0	28.1	27.6
10th–90th percentiles	37.5–241.3	5.1–59.5	7.5–53.3
Class mean (0.2)	133.0	28.1	27.6
Median	100.7	19.7	22.0
Soluble			
Range	ND–7.1	1.1–8.4	0.7–5.9
Arithmetic mean	3.1	2.7	3.2
20th–80th percentiles	1.0–5.7	1.1–3.2	1.9–4.2
Class mean (0.4)	3.0	1.7	3.1
Median	2.6	1.3	3.1
30 000–80 000 km			
Particulate			
Range	22.5–525.1	4.0–110.4	1.2–114.5
Arithmetic mean	161.8	37.3	27.0
10th–90th percentiles	55.5–260.0	7.7–69.8	7.9–43.0
Class mean (0.2)	148.3	33.8	24.0
Median	130.0	33.6	23.4
Soluble			
Range	0.3–53.6	ND–54.9	0.1–75.8
Arithmetic mean	7.0	13.7	7.7
20th–80th percentiles	1.4–9.1	1.5–21.9	1.0–10.2
Class mean (0.4)	4.6	10.6	4.8
Median	4.0	10.8	4.8

function, severe driving conditions and improper car maintenance. These factors can cause partial or complete destruction of catalysts, with consequently higher PGE release. Unpublished information from the catalyst manufacturers and automotive industry are indicative of a considerable amount of demolished catalysts (Hagelüken, 1995). The relatively high amount of PGE found in environmental samples (road dust, soil, plants, etc.) in comparison to the amount found in car exhaust fumes could be attributed to higher PGE release under real driving conditions.

The soluble Pt amount in exhaust fume samples of fresh gasoline and diesel catalysts is significant, but in most cases represents less than 10% of the total amount. Previous publications pointed out that the main releases of Pt into the environment from fresh gasoline catalysts are particulate and only 10% of the total Pt emissions are water-soluble (König et al., 1992). Our results seem to confirm this assumption. However, this is not the case for Pd and Rh, with releases in the same order of magnitude as the particulate, mostly in the 30 000–80 000-km range. However, no data for diesel catalysts have been reported in the literature.

The exhaust fumes from the Pd–Rh catalyst and the diesel catalyst labelled as ‘Pt only’ had relatively high amounts of other PGE in both soluble and particulate form. Although the gasoline B catalytic converter is a Pd/Rh catalyst, a Pt pre-catalyst placed in the front part of the can is reasonably responsible for the Pt amount found. However, a similar explanation cannot be given for the diesel catalysts. Moreover, the Rh concentration obtained by ICP-MS was checked by some laboratories by cathodic stripping voltammetry (CSV) with analogous results. No risk of contamination from the sample collector, connections used, or interference magnification were possible, because all the connecting tubes necessary were new and used only for the study.

Correlating release data with traffic data could give an approximate estimate of the total emission of PGE from cars while driving. Emission data taken from CEPLACA were applied to traffic statistics from Madrid (Spain) and Sweden, and the estimated global PGE release from diesel and gasoline cars is shown in Table 6. An interesting comparison can be made with German data, also based on engine test experiments (Kümmerer et al., 1999). A calculated amount of emitted Pt of approximately 10 kg per year for the whole of Germany can be considered to be in a range similar to that of Spain, if the figure obtained in the Madrid study is extrapolated to the whole country. Data obtained in Sweden are also in the same range, considering the low floating population of this country.

Table 6
Estimated global PGE release from gasoline and diesel cars running in Madrid (Spain) and Sweden

	Platinum	Palladium	Rhodium
Madrid (Spain)			
Total (g year^{-1})	610	390	190
Soluble (g year^{-1}) (% of the total)	60 (10)	160 (40)	80 (40)
Sweden			
Fresh catalysts	331	828	169
Moderately aged catalysts	252	631	252
Total (g year^{-1})	583	1459	421

Table 5
PGE in exhaust fumes collected from a diesel car fitted with a Pt catalyst (C_2)

	PGE (ng km^{-1})		
	Platinum	Palladium	Rhodium
0 km			
Particulate			
Range	23.3–87.3	1.0–8.1	2.9–13.3
Arithmetic mean	31.3	3.6	5.8
10th–90th percentiles	17.1–47.1	1.1–6.5	3.4–9.5
Class mean (0.2)	31.3	3.6	5.8
Median	24.1	3.3	4.6
Soluble			
Range	ND–5.8	ND–2.2	0.1–3.4
Arithmetic mean	1.4	1.2	1.6
20th–80th percentiles	0.1–2.9	0.5–1.9	0.1–3.2
Class mean (0.4)	0.7	1.2	1.5
Median	0.3	1.3	1.3
30 000–80 000 km			
Particulate			
Range	16.9–516.1	2.6–285.6	3.2–165.7
Arithmetic mean	126.3	58.4	31.1
10th–90th percentiles	33.5–263.0	10.7–131.1	7.3–63.8
Class mean (0.2)	108.9	44.6	24.8
Median	87.6	36.8	18.1
Soluble			
Range	0.6–72.0	0.9–54.4	ND–24.7
Arithmetic mean	8.8	17.4	6.3
20th–80th percentiles	1.6–15.0	3.0–29.9	1.3–10.2
Class mean (0.4)	5.3	14.0	4.4
Median	4.5	12.6	4.3

The toxicity of Pt and its compounds has been extensively reviewed by Lindell (1997). The acute toxicity of Pt compounds depends mainly on their solubility. Soluble Pt salts are much more toxic in animal experiments than compounds with low solubility, such as PtO, PtO_2 and $PtCl_2$. Several soluble Pt compounds showed mutagenic effects in bacterial systems (WHO, 1991), as well as in mammalian cells, but not in vivo in *Drosophila melanogaster* or in a mouse micronucleus tests (WHO, 1991). Toxicological data on Pd and Rh are scarce. For both $PdCl_2$ and $RhCl_3$, increased tumour incidences were observed in a lifetime drinking-water carcinogenicity study with mice (Schroeder and Mitchener, 1971). Only one case report of occupational asthma caused by Pd has been published (Daenen, 1999). Bünger et al. (1996) investigated the cytotoxic and mutagenic properties of industrially used compounds of Pt, Pd and Rh, and found that Pd and Rh salts were 3- and 30-fold less toxic, respectively, than analogous Pt complexes.

It is not clear if automotive-emitted PGE pose any human health risk, because there is controversy about the allergenicity of Pt, Pd and Rh emissions from car catalysts. The allergy-eliciting potential of Pt compounds is confined to the group of ionic complexes containing halogen ligands, and these halogen complexes are likely to be the main components of the soluble fraction of exhaust fumes due to high level of halogens present on the catalyst as a result of fuel additives. Furthermore, the emission of soluble or volatile PGE, probably as carbonyl complexes, cannot be completely excluded. The solubility of Pd and Rh emitted is higher than for Pt, and therefore more adverse effects can be expected for these elements.

Based on the results obtained in this study, the following points of major concern should be taken into account for subsequent studies:

- The first concern refers to the soluble Pd and Rh forms, which were found to be higher than expected and should be addressed in greater depth in the future, for instance, by using a different acid reagent to ascertain the real solubility of the more labile forms. The final fate of these forms is mainly river water, in which preconcentration and bioaccumulation could lead to a biomagnification process if concentration increase after this type of catalyst has been in use for several decades.
- Unfortunately, the sampling device could not collect any possible volatile forms of Pt, Pd and Rh. However, considering the reactivity of the ionic forms of these elements with carbonyl compounds, the possibility of the formation of volatile compounds cannot be ruled out and more research should be carried out in this area.
- The diesel catalyst differs from the gasoline catalyst with respect to the higher release of PGE. This technology should be improved, in particular considering that the number of diesel cars will substantially increase in the years to come.

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