

Platinum group elements in urban road dust

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Introduction of catalytic converter in our automobiles played a vital role in the reduction of harmful emissions such as carbon monoxide, volatile organic compounds and oxides of nitrogen. The three-way catalytic converter which consists of platinum (Pt), palladium (Pd) and rhodium (Rh; Pt–Pd–Rh), while reducing harmful emissions also increases the concentration of platinum group elements (PGEs) into the environment. This situation is due to the deterioration of the surface abrasion of the catalytic converter, thus releasing the PGEs adsorbed in small particles into the environmental compartments of air, soil and water. In this study, the concentration of PGEs in the environment was investigated using road dust collected from the city of Newcastle upon Tyne as a case study. The results obtained using ICP-MS revealed an elevated concentration in PGEs in the road dust in comparison to the lithospheric average. From the study, the average concentration is as follows: platinum = 38.23 ng/g, palladium = 79.8 ng/g and rhodium = 17.56 ng/g. The average concentration of PGEs in the lithosphere is 5.0×10^{-6} ng/g for Pt, 1.5×10^{-5} ng/g for Pd and 1.0×10^{-7} ng/g for Rh.

Keywords: Catalytic converter, lithosphere, platinum group elements, road dust.

THE platinum group elements (PGEs) comprise of iridium (Ir), osmium (Os), palladium (Pd), platinum (Pt), rhodium (Rh) and ruthenium (Ru). These are all transition metals lying in the d-block (groups 8–10, and periods 5 and 6). Platinum and palladium are found in their pure state in nature¹. The other four elements, Ir, Os, Rh and Ru occur as alloys of Pt and Au (gold). PGEs are mined in South Africa, Siberia and Sudbury, Ontario. The concentration of PGEs in the lithosphere is among the lowest, with the average estimated² to be in the range 0.001–0.005 mg/kg for Pt, 0.015 mg/kg for Pd, 0.0001 mg/kg for Rh, 0.0001 mg/kg for Ru, 0.005 mg/kg for Os and 0.001 mg/kg for Ir. Worldwide production of PGEs has been steadily increasing since 1970. This reflects the growing worldwide use of PGEs. Of the six PGEs, those interest for the present study are Pd, Pt and Rh, because of their use in the construction of catalytic converters used in automobiles. The properties of PGEs which make them suitable to be used as catalytic converters include: (i) outstanding catalytic properties, (ii) resistance to

chemical attack, (iii) stable electrical properties, (iv) high corrosion resistance, (v) low coefficient of thermal expansion, (vi) high melting point and (vii) high mechanical strength. PGEs released from the catalytic converters are primarily bound to aluminium oxide particle^{3,4}. Until recently they were regarded as inert elements, but recent studies have shown that they may be soluble and quite reactive.

The main emissions of automobile engines are N₂, CO₂ and H₂O. These emissions are mainly non-harmful to humans; however, because combustion is never perfect, smaller amounts of more harmful emissions are also produced, namely carbon monoxide (CO), hydrocarbons (HC) or volatile organic compounds (VOCs) and oxides of nitrogen (NO_x). These gases are the largest source of ground-level ozone which is responsible for smog formation, respiratory problems and damage to plant life. It is in this background that the catalytic converter was developed to convert the three main regulated emission gases to harmless products. All modern cars are fitted with a three-way catalytic converter (TWC). The three-way refers to the three regulated emissions it helps reduce—CO, unburnt HC and NO_x. The converter uses two types of catalyst: the reduction and oxidation catalysts. Pd and Pt are used as oxidation catalyst to oxidize CO and HC while Rh is used as a reduction catalyst to reduce NO_x (refs 5 and 6). While the TWCs (Pd–Pt–Rh) significantly reduce up to 90% gas emissions produced during gasoline combustion^{7,8}, they may at the same time create serious environmental problems. This situation is due to the deterioration of the surface abrasion of the catalytic converter, thus releasing the PGEs adsorbed in small particles into the environmental compartments of air, soil and water⁸. At present, there is no publication on the level of PGEs in road/urban dust in Newcastle upon Tyne. Hence the need for the present study so as to compare the concentration with those in the other parts of the world to ascertain the impact of TWC introduction into our automobiles.

Road dust/sediment samples (>10 g) were collected from nine different sites using hand-brushing with a plastic brush and plastic collection pan. This was achieved by sweeping with the brush and pan^{9,10}. Each brush and pan was considered disposable and used only once. A number of identical dustpan and brushes were used in the study and the sampling process was kept consistent in order to minimize sampling variability. The samples collected were put in a sample bag and dried in the oven at 40°C for several days. Then, the samples were passed through a plastic sieve of mesh size 250 μm to separate into <250 μm particle size fractions.

The reagents/chemicals used for this experiment include concentrated HCl and HNO₃ obtained from Romil Limited, Cambridge. A multi-element standard containing Ir, Pd, Pt and Rh was purchased from SPEXCertPrep (Middlesex, UK). Ultra pure water of conductivity

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18.2 M Ω -cm was produced by a direct QTM millipore system (Molsheim, France). A road dust certified reference material was used (BCR 723 No. 114), supplied by the Institute for Reference Materials and Measurements (Certified 2002, Revised 2008). Poly-prep chromatography columns and AG[®] 50W-X8 cation exchange resin 200–400 mesh size from Bio-rad Laboratories (Hercules, Canada) were used. An evaporating unit for Reacti-ThermTM heating models (containing Reacti-vapTM teflon[®]-coated needles 4" (102 mm) \times 19 gauge and Reacti-ThermTM heating module) and vortex mixer were from Fisher Scientific UK Ltd (Leicestershire). Other instruments were specimen tubes made of soda glass with stopper, retort stand with clamps, glass measuring cylinder (A-grade), volumetric flask (A-grade) and eppendorf micro-pipette. Dust samples were collected from locations across Newcastle city centre and local environs. Inductively Coupled Mass Spectroscopy (ICP-MS) measurements were carried out with an ICP mass spectrometer X series II (Thermo Electron Corporation, Cheshire, UK). All digestions were carried out using a Start D multiprep 42 high throughput rotor microwave digestion system supplied by Milestone Microwave Laboratory Systems, UK. The weighing balance used was Explorer Ohaus model E406 00032 from Switzerland.

All plastic containers used for the preparation of cation exchange resin and separation columns were soaked in an acid bath for about one week prior to the preparation. They were rinsed with ultra pure water and allowed to dry before being used. Then 250 g of AG 50-X8 200–400 mesh cation exchange resin was placed into a pre-cleaned 1 litre plastic container. Next 250 ml 6 M HCl was added to the container and shaken to allow mixing. This solution was allowed to stand overnight. The next morning the 6 M HCl was decanted from the mixture and replaced by 250 ml 8 M HNO₃. The new solution was shaken and allowed to stand overnight. The next morning the 8 M HNO₃ was decanted from the mixture and replaced by 250 ml 6 M HCl. This process of mixing and decanting 6 M HCl and 8 M HNO₃ was repeated three times. Then, the resin was finally stored in 250 ml 6 M HCl and was ready for use. The retort stands with the clamps were arranged such that the poly-prep chromatographic column was held tightly and in a convenient position. The entire set-up was kept in a well-secured place to avoid shaking and other forms of interference such as dust from external sources getting into the column. Once the column was set, 4 ml of freshly shaken resin was added to it and the solution allowed to drain through. Then 10 ml of 6 M HCl was added to the settled resin and the solution allowed to drain through, after which it was equilibrated using 15 ml of 0.5 M HCl. A pre-cleaned acid-washed specimen tube was placed beneath each column prior to loading of the sample.

The sample was digested using the microwave method by adding 20 ml of aqua regia (HCl : HNO₃ 3 : 1 v/v),

made from Romil acid and the temperature raised to 200°C for 10 min. This is because catalyst-derived particles which carry PGEs are usually in a form difficult to digest¹¹. The filtrate from the microwave aqua regia digest was vortex mixed and sub-sampled by removing 4 ml from each sample and blank. The sample and blank were evaporated to dryness under a stream of N₂ and heat. The residue was re-dissolved using 5 ml 6M HCl, evaporated in a stream of nitrogen and heat, and then re-constituted using 2 ml of 0.5M HCl. After re-dissolving the re-constituted residue, the solution was added to the cation exchange column. The low affinity of PGE-anion complexes for the cation resin indicates that they begin to elute almost immediately. The eluent is collected in pre-cleaned acid-washed specimen tubes made of soda glass with poly stopper. To the same residue, further 2 ml of 0.5 M HCl was added, vortex mixed and then poured to the cation exchange column. The eluent was collected in the same specimen tubes. Again 6 ml 0.5 M HCl was added to the column and the eluent collected in the same specimen tubes. The process of washing the residue in the column with 2 and 6 ml 0.5 M HCl was repeated. Experiments have shown that this is sufficient to wash all PGEs of interest off the column, while all major cations are retained (Al, Ca, Fe, K, Mg, Mn, Na and Ti)¹². The solution containing PGEs and other anion complexes from the column was evaporated to dryness under a stream of N₂ and heat. To the dry residue was added two drops 16 M HNO₃ to remove organics and then vortex mixed. This mixture was evaporated to dryness in a stream of N₂ and heat. The final residue was made up to 2 ml using 3% HNO₃, vortex mixed and stored in the refrigeration (4°C) for ICP-MS analysis.

The analytical method adopted here follows that of Sutherland *et al.*¹². The X series II ICP-MS was tuned using a 10 ppb solution of Li, Be, Bi, Ce, Co, In, Ba, Pb, Tl and U in 2% HNO₃ to verify mass resolution. The tuning was done in standard mode. Table 1 shows the conditions for standard mode.

Calibration standards ranging from 0.1 to 10 μ g/kg prepared from a multi-element standard (Ir, Pd, Pt and Rh) were used to calibrate the instrument. Table 2 provides the calibration data. Masses 103, 105, 106, 108, 110, 194, 195, 196 and 198 were measured in addition to masses 88, 89, 90, 95, 111, 114, 178 and 181, to correct for oxide interferences. Standard solutions of Hf, Sr, Y and Zr were run at the beginning of the analytical session to generate oxide production ratios that were used for on-line corrections. Samples were washed out with 1% HNO₃ for 3 min between each analysis. Instrumental drift was monitored by regularly running standard element solution between samples. Precision and accuracy were measured using certified reference material BCR 723 with certified concentrations of Pd, Pt and Rh. The soil samples and blanks were diluted with an appropriate dilution factor. The samples and the blanks were analysed

Table 1. Operating conditions for ICP-MS

Operating conditions	Nebulizer flow rate (l/min)	Pole bias (V)	Hexapole bias (V)	Focus	Forward power (W)	Resolution (m/Δm)
Standard mode	1.0	12	20	30	1150	10,000

Table 2. Calibration data for the platinum group elements (PGEs)

Element	Isotope	Calibration equation $y = mx + c$	Correlation coefficient (r^2)
Palladium	^{105}Pd	$y = 20713.1x + 2.5 \times 10^{-4}$	0.9999
Platinum	^{195}Pt	$y = 20345.4x + 5.3 \times 10^{-4}$	0.9999
Rhodium	^{103}Rh	$y = 128047.4x$	0.9999

Table 3. Concentration of PGEs in dust reference material BCR 723

Element	Measured value (ng/g)	Certificate value (ng/g)
^{105}Pd	4.8 ± 0.16	6.10 ± 1.9
^{195}Pt	75.5 ± 1.16	81.3 ± 2.5
^{103}Rh	8.6 ± 0.02	12.8 ± 1.3

using ICP-MS with reference material analysed after every eight samples.

Spectroscopic interferences are probably the largest class of interferences in ICP-MS and are caused by atomic or molecular ions that have the same mass-to-charge as the analytes of interest. The determination of PGEs using ICP-MS is associated with numerous interference problems. This spectroscopic interference, arising from major constituents of the sample, complicates PGE determination¹³. It is particularly severe when analysing catalytic converter pollution products due to the common use of Sr and Zr substrate in the catalysts, which generates unusually high and significant levels of oxide interferences on the PGE masses of interest¹². ICP-MS is used in the determination because of its multi-element capacity and the extent of the isotopic information one is able to produce.

The analytical isotopes ^{105}Pd , ^{195}Pt and ^{103}Rh were selected based on the natural abundances of the analytical isotopes and the ascertainment of relative abundances of the potential atomic and molecular interfering ions along with the resolution required to separate analyte masses from interfering masses¹⁴. Palladium has 105, 106 and 108 isotopes with abundances of 22.3%, 27.3% and 26.5% respectively. The isotopes 106 and 108 suffer from isobaric monoatomic interference of Cd ion, while ^{105}Pd does not suffer from any monoatomic ion interference; hence it is the chosen isotope for analysis.

Platinum 195 was chosen as the preferred isotope for measurement because it has the highest abundance (33.8%) compared to the other isotopes. Platinum 194 has abundance of 32.9%. Some of the interfering ions are quantitatively retained by the cation column relative to

PGEs, thus effectively separating them and causing reduced problems¹²; for example, $^{87}\text{Sr}^{16}\text{O}$, $^{86}\text{Sr}^{17}\text{O}$ for ^{103}Rh and $^{89}\text{Y}^{16}\text{O}$ for ^{105}Pd . Hf and Zr behave as anion complexes^{15,16} and hence elute with the PGE from the cation column causing serious interferences. Oxides of these elements interfere on the Pd mass spectrum with respect to Zr and in the Pt mass spectrum for Hf. Oxides of these elements were reduced by the use of a nebulizer, which maintains oxide generation levels below 0.05% of the total mass signal. Example, Zr signals of $>10^6$ cps produce $^{90}\text{Zr}^{16}\text{O}$ signal of 500cps or less, which can be easily corrected from PGE analyte signals that are normally $>10,000$ cps. Interferences linked to other metals, e.g. Cu, Zn and Pb can be separated in the resolution mode of 4000 cps, which is well below that for PGEs of 10,000 cps (ref. 17). Interferences not separated from instrumental manipulations and treatment stages were corrected mathematically by estimating the contribution of interfering species to the PGEs signal through the analysis of single-element standard solutions of interferents^{17,18}.

Validation was performed by analysing dust reference material BCR 723. For this, 0.5 g of the Certified Reference Material (CRM) was prepared using microwave digestion. Table 3 shows the results of the analysis. The results show that there is good agreement between the measured value and the certificate.

Figure 1 shows the Pt, Pd and Rh concentrations in road dusts from Newcastle city centre.

The range of Pd, Pt and Rh concentrations from road dust is 2.70–203.7, 8.1–118.5 and 1.2–54.8 ng/g respectively, with mean concentrations of 79.8 ng/g for Pd and 38.2 ng/g for Pt and 17.6 ng/g for Rh. The mean value of Pd is significantly higher than those of Rh and Pt. This is not surprising, as there is a widespread shift in the development of catalytic converter technology away from Pt towards Pd as the main catalytic component¹⁹. Samples 11, 13 and 19 exhibit the highest concentration of Pd contributing 28.4%, 23.2% and 26.1% respectively, of the total PGE concentration. The highest concentration of Pt is found in sample 18 contributing 34.5% of the total concentration of PGE in the sampled area. The results obtained from Newcastle are compared with those of other cities in the world, as shown in Table 4. Mean Pt concentration in Newcastle dust sample (38.2 ng/g) is comparable to those from Ioannina, NW Greece (3.2–306 ng/g)²⁰, Scotland (13–335 ng/g)²¹, and Rome, Italy (14.4–62.2 ng/g)²². Mean Rh concentration (17.9 ng/g) in this study compares favourably with those of Bialystok, Poland (19.6 ng/g)²³, Perth, Australia (8.8–91.4 ng/g)¹⁹

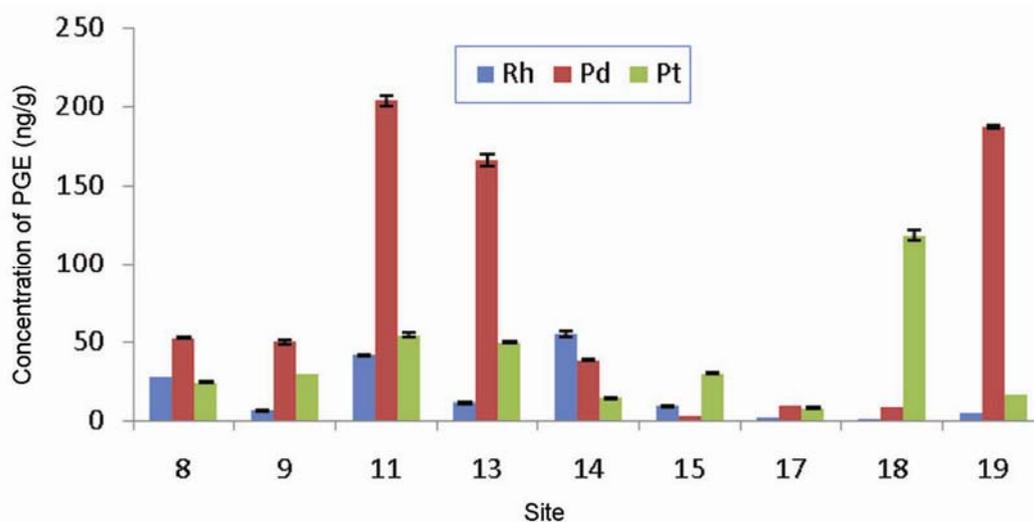


Figure 1. Platinum group elements (PGEs) concentration in road dust in Newcastle upon Tyne city centre.

Table 4. Global concentration of PGEs in road dust (ng/g)

Location	¹⁰⁵ Pd	¹⁹⁵ Pt	¹⁰³ Rh	Reference
San Diego, USA (1985)	38–280	100–680	–	24
Germany (1995)	1–146	–	–	23
Japan (1987)	297	–	–	27
Frankfurt (1995)	–	170	–	28
Richmond, UK (2001)	–	0.42–29.8	–	26
Nottingham, UK (1998)	92.9	168.5	–	29
Birmingham, UK (1997)	–	6.48	–	29
London, UK (2000)	–	73.7	–	30
Styria, Austria (1994)	4.0	55	10.3	31
Dortmund, UK (1993)	–	12	–	32
Graz Austria (1986)	–	14.5	–	24
Belgium (1996)	–	12.04	–	33
Rome, Italy (2000)	102–504	14.4–62.2	1.9–11.1	22
Goteborg, Sweden (2000)	80	196	93	16
Madrid (2001)	–	317	74	26
Scotland (2002)	–	13–335	–	21
Bialystok, Poland (2002)	36.6	–	–	31
Bialystok, Poland (2004)	37.5	110.7	19.6	23
Perth, Australia (2003)	58.1–440.4	53.8–419.4	8.8–91.4	19
Ioannina, NW Greece (2009)	2.1–18.2	3.2–306	6.1–64.6	20

and Ioannina, NW Greece (6.1–64.6 ng/g). Mean Pd concentration (79.8 ng/g) is similar to those reported in San Diego USA (38–280 ng/g)²⁴, Germany (1–146 ng/g)²⁵, Perth, Australia (58.1–440.4 ng/g)¹⁹, and Goteborg, Sweden (80 ng/g)²⁶.

Thus PGEs (Pd, Pt and Rh) from the nine sampled sites in Newcastle city centre indicate a strong anthropogenic signal. Both the global concentration and the results from the present study reveal that the introduction of catalytic converter to our automobiles in the process of reducing the harmful emissions from the exhaust has resulted in the increase of PGEs in our environment. The impact of this elevated PGE concentration is beyond the scope of the present study.

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