Impact of automobile emissions on the levels of platinum and lead in Accra, Ghana

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Examination of car fleet records in Accra demonstrates an increasing proportion of catalytic converter-equipped cars in the relatively old car fleet (average age 13 years) due to their import from developed countries. However, only leaded petrol is sold in Ghana. Lead *anti*-knocking additives, which are known to affect catalyst activity and promote thermal sintering and mechanical abrasion, may increase Pt emissions. This possible synergism prompted the concomitant determination of Pb and Pt levels in road dust and roadside soils in Ghana. Both metals followed traffic density with higher concentrations in urban areas compared to remote sites. In urban areas, the range for Pb (365 $\pm$ 93 μg g^{-1} for dust and 291 $\pm$ 76 μg g^{-1} for soil) reflects pre-catalyst levels in Europe and the US, while the range for Pt (39 $\pm$ 24 ng g^{-1} for dust and 15 $\pm$ 5.3 ng g^{-1} for soil) is typical for the same countries. The elevated Pt concentrations were unexpected due to recent introduction of catalysts to Ghana compared to the prolonged use of catalysts in Europe and the US.

1. Introduction

Automotive catalytic converters utilising platinum group elements (PGE) as their main active component were introduced in the US in 1975 in response to environmental initiatives that sought to decrease emissions of vehicular pollutants and improve urban air quality.[1] The first pellet catalysts oxidised hydrocarbons and carbon monoxide, employing various combinations of platinum and palladium. The addition of rhodium in a honeycomb matrix established the technology currently fitted to petrol engine vehicles today: the three-way catalyst (TWC). TWC differ from older oxidation catalysts in that they are also able to perform the reduction of nitrogen oxides.[1] The mandatory installation of catalytic converters in the US prompted their introduction in other developed countries and today, approximately 500 million cars are equipped with catalytic converters worldwide.[2]

It has been demonstrated that PGE are released from catalytic converters during vehicle operation.[3,4] While background and current levels in the environment are low, the full implications of these potentially allergenic and toxic metals accumulating in various environmental compartments is not clear.[5] PGE are difficult to determine accurately at environmental levels, but researchers have evidenced the presence of PGE in several media, including aerosols,[6,7] soils,[8] road dusts,[6,9,10] vegetation[8,11] aquatic sediments,[12,13] and macro-invertebrates.[13]

Until recently, research has only focused on environmental PGE levels in Europe, North America and Japan where catalytic converters have been required by law on newly manufactured vehicles for a decade or more.[5] The assessment of PGE levels elsewhere was prompted by the research of Barbante *et al.*[2] who detected PGE in the arctic environment. Based on fluctuations in PGE concentration, the presence of Pt, Rh and Pd was attributed to releases from vehicles rather than metallurgical refinery activities. The possibility that PGE are being transported globally has highlighted the need for expanding monitoring locations.

PGE loss from catalytic converters is mainly due to thermal sintering, evaporation and mechanical or thermal abrasion;[14] this loss is intensified by unfavourable operating conditions.[15] Ageing is also accelerated by impurities and additives in fuel, perhaps the most significant of these being lead.[16]

Tetraethyllead was first added to petrol to reduce knocking in the engine. Research on the effects of lead on catalytic converters showed that even trace amounts of Pb in petrol (less than 0.018 g l^{-1}) affect catalytic converter efficiency through the formation of a coating on the catalyst surface.[17] Analysis of catalytic surfaces established that there is fouling by lead even in catalysts where unleaded petrol is used.[18] The use of tetraethyllead in fuel necessitates the addition of halogen-based scavengers that transport lead out of the engine and it was postulated that the lead halides leaving the engine decompose on Pt with the volatile halogen desorbing, leaving the resulting Pb species to accumulate.[16,19] In developed countries both the impact of lead on catalytic converters and concern over potential human health effects have prompted the phase out of leaded petrol.[20]

This is the first evaluation of platinum and lead levels in a developing country where the use of catalytic converters is not regulated and lead is still used as a petrol additive. The study focussed on Pb and Pt levels in collected road dusts and soils and includes an inventory of the number of catalytic converters in Accra, Ghana.

2. Materials and methods

2.1 Study site

Ghana is one of the most densely populated countries in West Africa. It has a population of 18.8 million people, with 1.3 million people in Accra. The climate is tropical and there are

Table 1 Sampling site description

Site No.	Site name	Cars per day	Location	Particulars
1	Background	0	Remote village	200 m from road behind dwellings
2	Village	200	Remote village	Along road with continuous traffic
3	Residential	500	Residential area	Some road cleaning, road dust sample from gutter with continuous traffic
4	Highway	4000	Two lane coastal highway	Along road with high speed continuous traffic
5	Airport	5000	Kotoka international airport	Along road with stop and go traffic

two distinct rainy seasons: May–June and September–October. The average humidity is $\pm 80\%$ the year through and temperatures range between 25 °C and 29 °C.

In Ghana, as in many developing nations, environmental issues have a low priority due to the lack of financial resources. While there exists no formal environmental policy for air quality in Ghana, the government banned the import of vehicles older than 10 years of age between 1998 and 2002; currently there is a heavy import tax on older vehicles. The phase out of leaded fuel has already been called for in 25 sub-Saharan nations in the World Bank Institute's Clean Air Initiative,[21] but to date only leaded fuel is available in Ghana.[20]

2.2 Car fleet investigation

To get a better idea about PGE emissions in Accra and to aid in future investigations, data on the car fleet was gathered. Data was acquired by interviews with the general public and from the Driver and Vehicle Licensing Authority (DVLA) in Accra. The DVLA was able to supply information on the number of vehicles registered in the city and allowed access to their registry books. Several assumptions were made in order to estimate the number of cars equipped with catalytic converters based on data taken from the DVLA, including manufacturers' home location, or known years of production of a particular vehicle and the possible age range of the car fleet. In the event of any uncertainty in deciding if a car was catalytically equipped or not, it was recorded as being non-equipped.

2.3 Sampling

Sampling took place at five locations in and around Accra during September and October 2001. Sites were selected based on their traffic intensity and ease of sampling (Table 1). Road dust samples were taken using a brush and spatula. A 1 m strip was sampled 20 cm from the side of the road. Soil samples were taken from the top 5 cm of soil. All samples were stored in plastic containers until further treatment.

2.4 Sample preparation

Samples were dried at 105 °C for 24 h and sieved into two size fractions: <63 μm and >63 μm. Only the smaller size fraction was analysed for comparative purposes. Aliquots of 250 mg were placed in sealed PTFE vessels (HP500) together with 8 ml of *aqua regia* ($HCl:HNO_3$ 3 : 1 vol : vol). Suprapure subdistilled 65% HNO_3 and 30% HCl (Prochem AB, Ulricehamn, Sweden) were used. The samples were mineralised in a CEM Mars 5 (CEM, Mattheus, USA) microwave digestion system with stepwise increase of temperature and pressure (Table 2). After digestion samples were heated to dryness in glass beakers and the residue was dissolved in 2% HCl. This solution was kept frozen in PET tubes until analysis.

Table 2 Program for microwave digestion

Stage	Attempting temperature/°C	Maximum pressure (psi)	Ramp/min	Holding/min
1	110	50	5	2
2	140	100	5	2
3	170	200	5	2
4	200	300	5	6

2.5 Sample analysis

Samples were analysed by quadrupole ICP-MS (Elan 6000, PE Sciex, Canada) with the settings given in Table 3. Lead and Pt were quantified using isotopes 208 and 195, respectively. The determination of Pd and Rh was not possible owing to the high concentration of interferents in the samples. Interferences caused by HfO^+ in Pt determination were corrected using eqn. 1, where I_{Pt} is the corrected Pt intensity, $I_{Pt,s}$ is the apparent Pt intensity in the sample, $I_{Hf,s}$ is the Hf intensity in the sample and $R_{HfO,Hf}$ is the ratio of HfO^+/Hf^+ determined by Hf standards.[7,13]

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

Interference was carefully considered by measuring Hf and checking the apparent concentration to corrected concentration ratio for all samples. Samples for which this ratio was larger than 3 were excluded from statistical analysis. Quality control for Pt determination was through participation in the certification of PGE concentrations in a tunnel dust reference material (European project PACEPAC). The platinum concentration was 79.7 ± 1.6 ng g^{-1}, in agreement with results from other laboratories involved.

3. Results and discussion

3.1 Car fleet

Nearly all cars in Ghana come from Europe through private sales or commercial operations. In Accra cars are usually imported at 8 years of age and not driven much beyond their 20th year, having an average age of 13 years. Three years previous to this study there was a complete ban on the import of cars older than 10 years.

DVLA tabulations of the total number of vehicles registered in the Greater Accra Region are given in Table 4. Data collection from DVLA registry books proved to be difficult as records are not as of yet computerised and the information was often incomplete. The registry books did not include the manufacture year so several assumptions were made in order to make an approximation of the number of catalytically equipped cars in the area. For cars with unknown manufacture year, the age was estimated to be 13 years, based on interview information. Best estimates place the number of catalytically

Table 3 Setting for ICP-MS used in sample analysis

Parameter	
Carrier gas and flow rate/l min^{-1}	Ar: 0.86
Plasma gas and flow rate/l min^{-1}	Ar: 16
Auxiliary gas and flow rate/l min^{-1}	Ar: 0.9
RF Power/W	1000
Data acquisition	Peak hopping
Dwell time/s	100
Sweeps per reading	10
Replicates	6

Table 4 Total number of vehicles in a given category as tabulated by the DVLA, Greater Accra Region up to the year 2000

Vehicle type	Total No.
Motor vehicle up to 2000 cc	314 733
Buses and coaches	83 614
Trucks up to 24 tons	51 954
Total vehicles in Accra	450 301

equipped vehicles in Accra at an upper end figure of 71.2% and the number of diesel vehicles at 19.7% based on a sample number of 4 285. Diesel vehicles are however not expected to be equipped with catalysts, as it is a relatively new technology.[1] These percentages translate to an estimated 300 000 cars equipped with catalysts and 90 000 diesel engine vehicles on the roads in and around Accra. It is a by-product of the Ghanaian vehicle import system that many cars in Accra are catalytically equipped.

3.2 Platinum in road dusts and soils

Sampling sites were chosen for their different traffic intensities. Platinum concentrations in road dust increased with increasing traffic density (Fig. 1a). This agrees with recent work by Moldovan *et al.*[4] Background Pt levels were higher than established crustal concentrations of 0.4 ng g^{-1}[22] having a range of 0.7–2.8 ng g^{-1} and a mean value of 1.5 ng g^{-1}. The mean background value is somewhat higher than background values reported in Europe[6] where background concentrations are typically below 1 ng g^{-1}.

Current Pt levels in road dusts in and around Accra agree with recent studies in Europe.[6] This was an unexpected finding as present-day Pt levels in Europe are the result of two to three

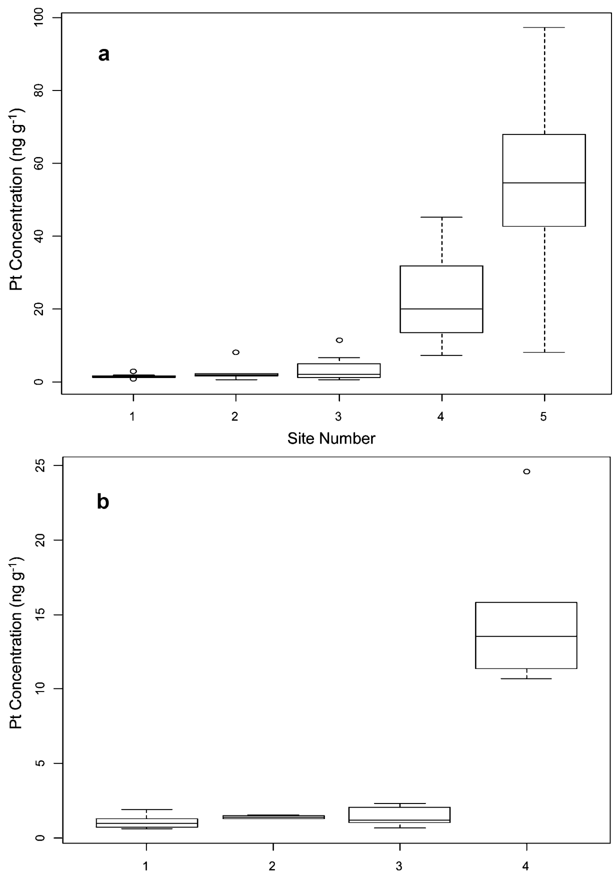

Fig. 1 Platinum concentrations in road dust (a) and soil (b) at five different sampling sites with increasing traffic density (Background (1) < Village (2) < Residential (3) < Highway (4) < Airport (5)).

decades of catalytic converter use. Petrucci *et al.*[23] found a range of 14.4 to 62.2 ng g^{-1} Pt at high traffic sites. Jarvis *et al.*[24] found a range of 10–100 ng g^{-1} at a roadway experiencing about 17 000 cars a day. The highest traffic density in this study was found at Kotoka International Airport with approximately 5 000 cars a day and a mean Pt value of 55.0 ng g^{-1}.

These findings can be explained by:

(i) Higher natural levels due to the mineral rich soils of Ghana.

(ii) The aged car fleet which may result in larger Pt releases. While Pt emissions from petrol engine catalytic converters have been reported to decrease with mileage,[4] emissions studies are performed under optimal engine conditions and do not accurately portray reality for which emission rates are believed to be higher by one to two orders of magnitude.[15] This is especially true in Ghana, where the economic situation results in low car maintenance with replacement parts coming from older, discarded vehicles. Even minimal ignition malfunctions can increase Pt emissions.[15] Furthermore, unpublished data from the catalytic and automotive industry demonstrate that it is not uncommon for catalysts to be destroyed due to mechanical and thermal impacts, sometimes leaving only pieces or none of the monolithic catalyst behind.[25]

(iii) The strenuous driving conditions in Accra may result in increased Pt release from automobiles. In and around Accra there is poor traffic flow and driving speeds are unregulated; both of these conditions contribute to higher Pt emissions.[3,26] Other factors such as poor driving surfaces, overloading of vehicles and low fuel quality are highly relevant to Pt levels in the study area.

(iv) Diesel catalytic converters show increasing Pt emissions with age. This catalyst type has only been commercially available since 1991.[4] The number of diesel catalysts is not likely to be significant due to the time lag in the vehicle fleet relative to Europe, but those present would be releasing significant amounts of Pt by virtue of their age and the factors discussed above.

Soil platinum concentrations generally adhered to changes in traffic density with background sites and residential sites having a lower concentration than urban sites (Fig. 1b). Platinum concentrations were higher in road dusts than in soils, which agrees with dispersion from road dust to other environmental compartments.[9] Samples were taken from the top 5 cm of soil less than 0.5 m from the road. Past studies have found that it is at this depth and distance that the greatest Pt concentrations are found.[24,27] Concentration ranges in this study were similar for equivalent sites in other publications with mean values between 1.1 and 1.4 ng g^{-1} for the more remote sites and 14.9 ng g^{-1} for high traffic sites. Alt *et al.*[8] analysed cultivated and roadside soils and found ranges of 0.15 to 3.9 and 15.6 to 31.7 ng g^{-1}, respectively. Zereini *et al.*[26] found concentrations in soils in Germany along major motorways to be in the range of 23 to 112 ng g^{-1}.

The majority of platinum is emitted as a nanoparticle of Pt(0) attached to aluminium oxide, which can be sourced back to the catalytic converter washcoat. It is believed that some Pt is emitted directly from the converter in a soluble form. Suggested levels of soluble emitted platinum range from less than 1%[27] to 10%[4] based on test bench studies. In addition, a fraction of the emitted Pt becomes bioavailable through environmental transformations of the metallic species. Wei and Morrison[28] found that the transformation of Pt as an inorganic to an organically bound species may occur. Lustig *et al.*[29] propose that humic substances can oxidise Pt(0), possibly forming organometallic complexes. These complexes may be immobilised by the soil through absorption to soil minerals, in particular clay-like elements. The soils in southern Ghana however, are poor in organic content and clay elements.[30] It is possible that Pt is oxidised on the surface of the soil. Then, due to the high porosity and leaching rate of ferrasols, Pt compounds are easily dispersed within the soil. If vegetation or soil fauna do not take the available platinum species up, ground and surface waters move them to aquatic sediments where they are either immobilised or incorporated into aquatic food webs.

Several other factors influencing Pt solubility should be mentioned.

(i) Pt solubility has been found to increase with decreasing pH.[26] Jarvis *et al.*[24] found increasing catalytic Pt solubility with time in simulated rain with a pH of 5.5. Ferrasols are acidic in nature with a pH at the surface of 5.0.[30] In addition soils in West Africa have been found to be at risk to further acidification caused by anthropogenic activities like agriculture.[31]

(ii) Sulfur increases the solubility of Pt in soils.[26] The fuels used in Ghana are higher in sulfur than those found in Europe. This sulfur would be emitted to the environment at the same time as any Pt affecting its solubility.

(iii) The size of the particle emitted is affected by the age of the catalytic converter. Artelt *et al.*[27] found indications of increasing emission in the smallest size fraction with age. It has been shown that there was a greater amount of soluble Pt in soils when smaller particle sizes were used.[29] This is likely due to the greater surface area available for reaction. Unpublished data for Pt concentrations in grass taken from Accra indicates that there is indeed a higher uptake than that found in Europe. However, comparisons between the two locations are complicated by factors which include length of growing season, climate, bacterial activity and plant morphology.

3.3 Lead in road dusts and soils

Vehicular emissions account for some 90% of all atmospheric lead emissions and is the largest source of human exposure in many areas.[20,32] The lead content of the petrol sold in Africa is the highest in the world. However, lead content in petrol available in Ghana is moderate in comparison with other African nations, with concentrations of 0.6 g l^{-1}. Combined with a petrol consumption of 400 Mtonnes a year, this equates to 300 tonnes of lead a year being used in petrol.[33]

Environmental Pb concentrations in road dusts increased with increasing traffic density (Fig. 2a). Comparisons with other studies are difficult as size fractions selected vary for the determination of lead in road dusts. Wei and Morrison[34] did use the same fraction however and found an average lead concentration in road dusts in 1984 in Sweden, just one year after the complete ban on leaded petrol in this country, to be 326 $\mu g\ g^{-1}$. Samples were also analysed from 1991 with a mean concentration of 182 $\mu g\ g^{-1}$. The results from 1984 are comparable to those found in Accra in 2001. Pb levels in soil samples also generally adhered to changes in traffic density (Fig. 2b).

It is not surprising that both trends for Pt and Pb follow traffic density; concentrations of traffic emitted metals tend to vary in a similar fashion.[35] Both metals are known to be emitted from vehicular sources albeit with differing release characteristics: Pb is emitted during combustion whereas Pt is principally released as particles.

As leaded petrol is no longer an issue in the developed world there has been little interest in exploring such emissions and research on Pb poisoning of catalysts has not addressed the effect of Pb on Pt emission. The main question raised by the research presented here is whether or not these two metals act in a synergistic fashion. There is some suggestion that Pb and different PGE are able to form alloys.[19] This may contribute to higher Pt releases amplifying the effects of this metal, perhaps even increasing the uptake by biota. To be considered also is the formation of halogenated Pt salts, which are proven harmful causing respiratory sensitisation and allergenic reactions. Moldovan *et al.*[4] theorise that these halogen complexes are likely to be part of the soluble fraction of exhaust fumes due to the fact that there are high levels of halogens present because of fuel additives. This study was done using European fuels, thus lead free and with a lower halogen content than that found with the leaded fuels in Africa. If this idea is proven true there is a greater possibility for Pt to be released as its soluble form.

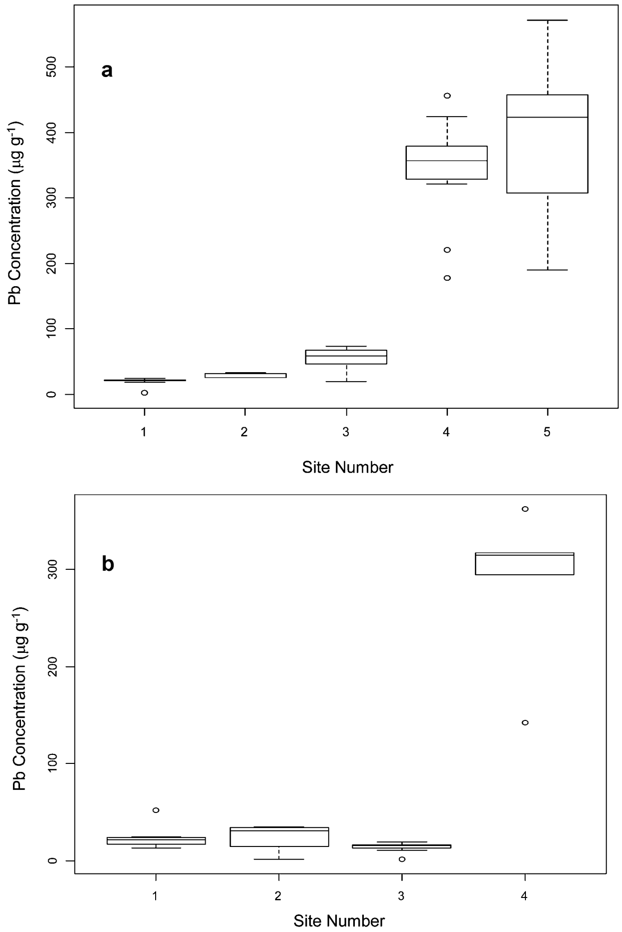

Fig. 2 Lead concentrations in road dust (a) and soil (b) at five different sampling sites with increasing traffic density (Background (1) < Village (2) < Residential (3) < Highway (4) < Airport (5)).

Conclusions

The number of catalytically equipped vehicles in Accra is increasing with replacement of the car fleet and leaded petrol remains the only fuel available. Pt levels in Accra were found to be similar to those currently found in Europe. This was an unexpected finding. The large discrepancy between test stand releases and environmental Pt levels can be explained by the fact that real operating conditions are rarely optimal. Accra provides an extreme, although common for developing country cities, example of undesirable operating conditions.

Both Pt and Pb concentrations were found to increase with increasing traffic density suggesting a vehicular source for both metals. The determination of Pd and Rh would aid in confirming this fact and in exploring other sources (*i.e.* distinguishing between petrol or diesel vehicles and natural sources). There is some indication that Pt may be more bioavailable in Southern Ghana because of soil characteristics and environmental variables. Of particular concern is the acidic nature of the soil. Acidification may progress with agricultural activities, which is the main occupation of some 90% of the Ghanaian population. Food has been suggested as a main pathway of Pt into man.[8]

While the phase out of leaded petrol has been called for by several key worldwide agencies, including WHO, WBI and

UNEP, there is some commercial resistance to this action.[36] The adverse health impacts of lead are well established.[33] There is a possibility that Pb and Pt act in a synergistic fashion and if this is found to be the case, it is yet another justification for the removal of leaded fuel from sub-Saharan Africa.

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