

The impact of vehicular fallout on the Pra estuary of Ghana (a case study of the impact of platinum group metals (PGMs) on the marine ecosystem)

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Abstract It is increasingly being recognised and environmental measurements have demonstrated that Platinum (Pt) (and potentially Rhodium (Rh) and Palladium (Pd)) is released with the ageing of catalytic converters. Platinum is a particular concern as it has a known mutagenic and toxic effect, even at exceedingly low concentrations, in urban air (affecting human health) and urban water (affecting ecosystem health). In the context given above and given the still keen lack of reliable experimental data on the levels of Pd, Pt and Rh in water and sediment, this study determined the concentration of such elements in water and sediment of the Pra estuary in the Western Region of Ghana where it is estimated that more than two thousand cars pass over the bridge under which the river flows to join the sea each day. Elevated concentrations of platinum (Pt), palladium (Pd) and Rhodium (Rh) were found to be associated with water and soils from areas of high traffic densities (Beposo) suggesting that vehicles also contribute heavy metals (PGMs) to the environment. The result showed elevated levels of these metals in river bank, waterbed and in the water. There is

therefore the tendency of possible accumulation of these metals in plant and animals along these areas.

Keywords Catalytic converters · Platinum group metals (PGMs) · Canberra Multi-Channel Analyzer (MCA) · Pra estuary · Kakum · Akotokyir · Beposo · Bosomdo Krobo · Shama Beach

Introduction

The impact of human activity on the environment is global, with the effects of chemicals in air and water spanning political and natural boundaries. An understanding of this impact is essential within and beyond the study of chemistry.

In an attempt to reduce air pollution caused by the emission of carbon monoxide, hydrocarbons and nitrogen monoxide by automobile exhausts, regulations have been put in place since the 1970s requiring that catalytic converters be fitted to all new motor vehicles (EPA 2000). A Catalytic converter is an air pollutant abatement device that removes pollutants from motor vehicle exhaust, either by oxidizing them into carbon dioxide and water or reducing them to nitrogen gas.

Catalytic converters use platinum group metals (PGMs); specifically platinum, palladium, rhodium; to rapidly oxidize exhaust emissions into less harmful substances. The burning of fossil fuels is generally a very clean reaction, meaning, it does not create much

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pollution if properly done. However, when combustion occurs with either too little or too much air, dangerous chemicals are produced, such as carbon monoxide, nitric oxide and sulphur oxides. Catalytic converters aid in the transformation of these pollutants into less harmful substances, like carbon dioxide and water etc. On the basis of documented evidence produced to date, it is generally accepted that the

thermal and mechanical conditions under which such devices work including abrasion effects and hot-temperature chemical reactions with oil fumes can cause significant release of the PGMs to the environment and eventually affect human health (Hodge and Stallard 1986; Helmers et al. 1994). The total extents of the emission, its composition in terms of relative concentrations of these elements, and the average size

Fig. 1 Map of the Pra Estuary (sampling site)

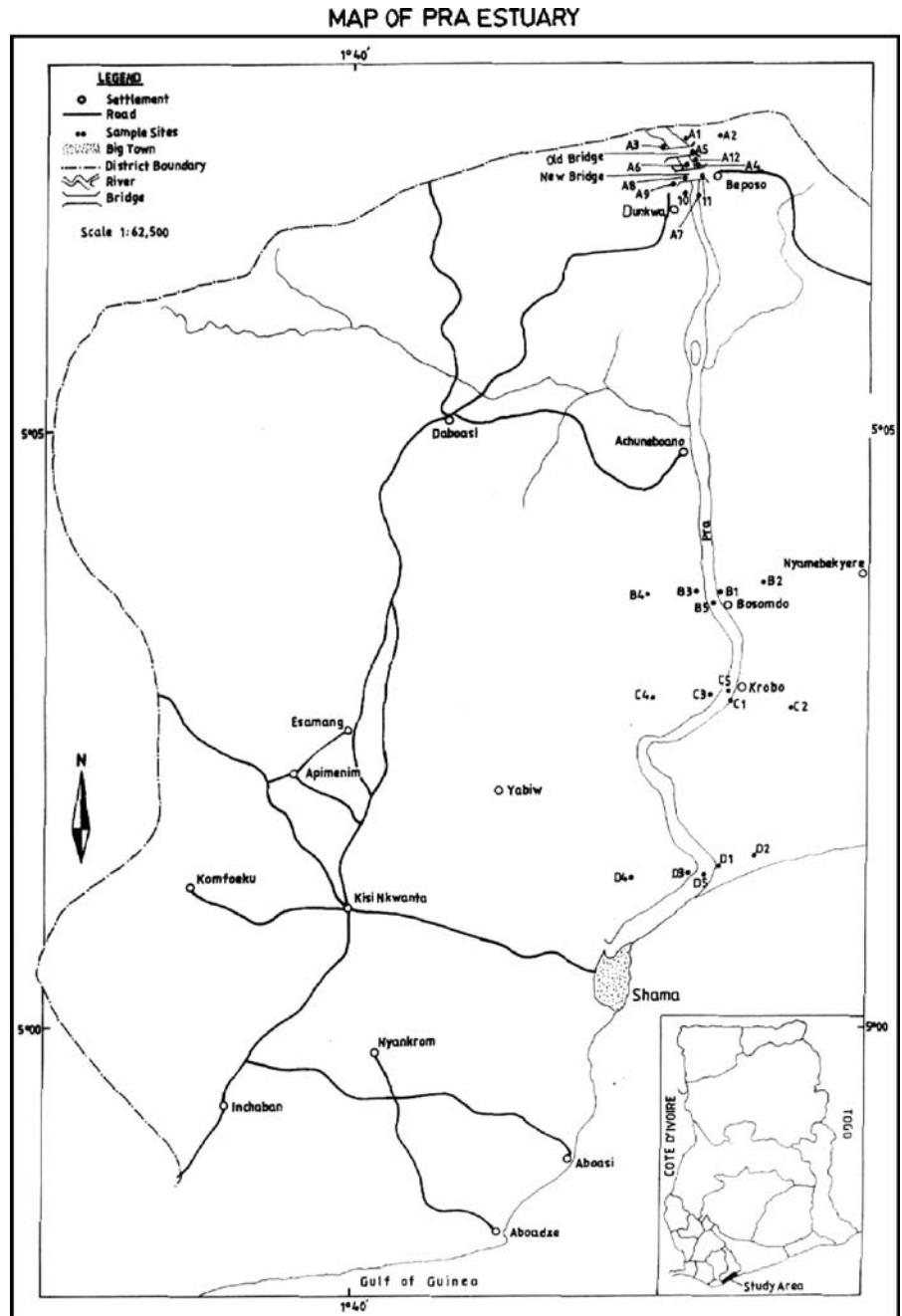
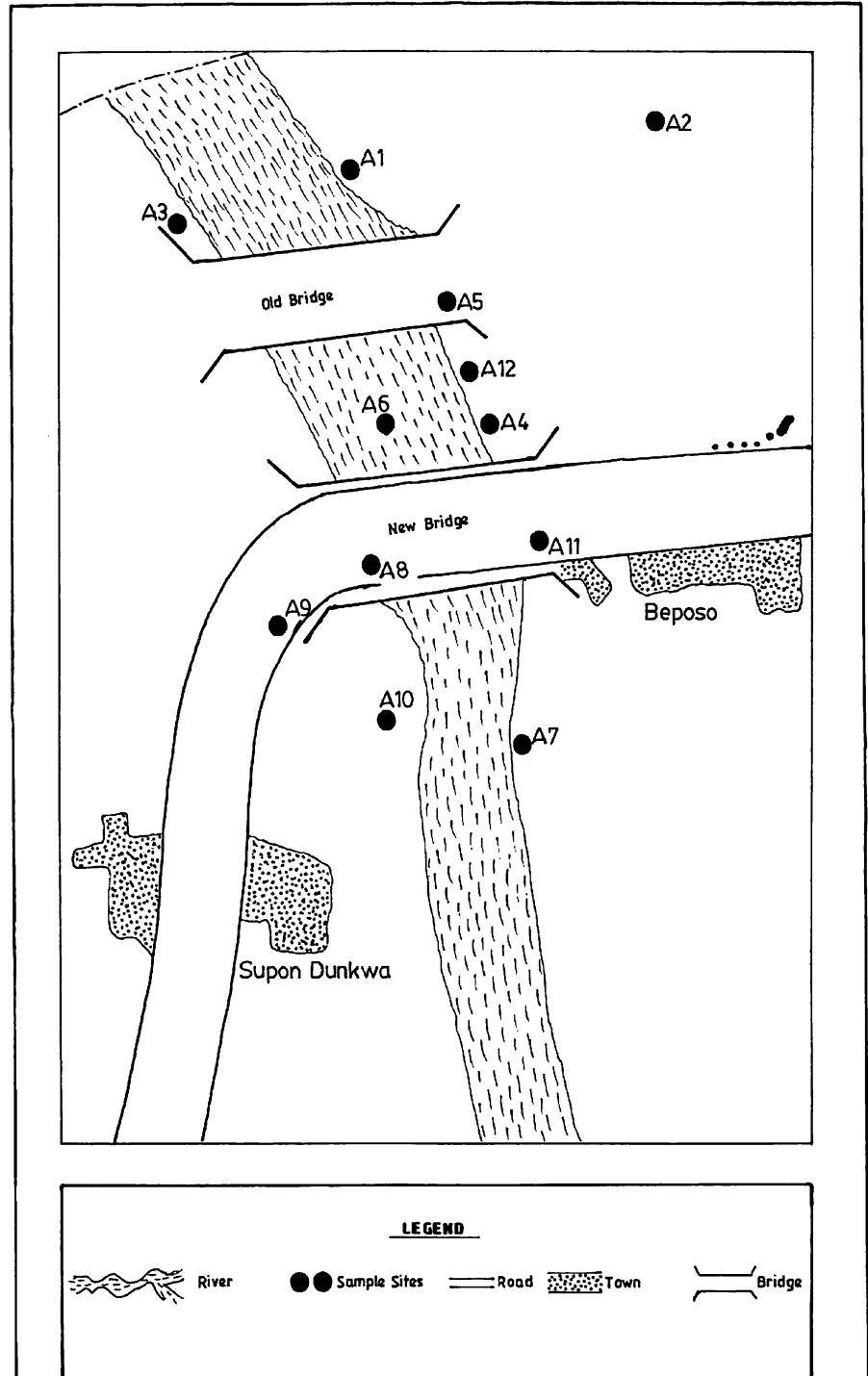


Fig. 2 Map of the Pra Estuary (the bridge)

FIG. 2 MAP OF PRA ESTUARY



of the emitted particles, strongly depend on the catalytic converter type and traffic conditions. This is still a highly controversial issue in that, e.g. the estimated release of Pt is reported to range from a few ng km^{-1} to several $\mu\text{g km}^{-1}$ when the car has a speed of 50–100 km h^{-1} , although the age of the catalytic converter may in part account for such discrepancies (Känig et al. 1992).

Ghana has no significant domestic assembly of motor vehicles and thus relies exclusively on imports. Used vehicles (5–10 years old) constitute about 70% of Vehicles imported into Ghana (U.S. Commercial Service 2006), however; this situation raises fears of possible deposition of PGMs in our environment (water bodies and soil along the roadways). This deposition will lead to increase concentrations of PGMs in the environment, raising concerns about the environmental impact and toxicity effect of these elements (Barefoot 1997). Studies conducted in developed countries such as Japan, United States of America (USA), etc. have revealed that the concentration of platinum in soils along highways ranged between 50 $\mu\text{g/kg}$ and 0.5 $\mu\text{g/g}$, whereas the crystal abundance of Pt in soil is about 1.5 $\mu\text{g/kg}$ (Nriagu and Pacyna 1988; Siva et al. 1990). Barbante et al. (2001) recently reported an increase in PGMs in snow samples from Greenland. Although the amounts measured were low (ng/kg range), concentrations were found to be 40 to 120 times higher for snow dated in the 1990s compared to ice samples dated 7,000 years ago (Barbante et al. 2001).

The concentrations of PGMs in river samples and roadside soils have been reported to be considerably higher (typically $\mu\text{g/kg}$ range) (Ranch et al. 2000). In 1991 the International Program on Chemical Safety (IPCS 1991) disseminated evaluations of current, limited data on environmental, epidemiological, toxicological effects, experimental laboratory testing and risk assessment on platinum. In roadside

dust deposited on broad-leaved plants at various sites in California, concentrations of 37–680 $\mu\text{g/kg}$ (dry weight) were detected (IPCS 1991). Analysis of sediment cores (1–20 cm) in Lake Michigan recorded concentrations of 0.3–0.43 $\mu\text{g/kg}$ dry weight (IPCS 1991). Samples of plants from ultra basic soil contained 100–830 $\mu\text{g/kg}$ of (dry weight). Blood platinum levels of 0.1–2.8 $\mu\text{g/L}$ have been found in the general population, while it has been reported that blood serum from occupationally exposed workers contain levels of 150–440 $\mu\text{g/L}$ (IPCS 1991). All these findings are evidence of the gradual accumulation of the metal which calls for investigations into its deposition since in Ghana no quantification data on PGMs in river sediment is known.

The long-held belief that PGMs are generally harmless stems from their chemical inertness. On the other hand, their role as sensitizers in the etiology of allergic pathologies such as: asthma; conjunctivitis; dermatitis; rhinitis; and urticaria have been thoroughly ascertained (Rosner and Merget 1990). In turn, Pt is a well-known cytotoxic agent, widely used in several anticancer drugs (e.g. Cisplatin and Carbo-platin), for the treatment of a number of malignancies (Dominici et al. 1989; Ensslin et al. 1994). Tumor cells are more prone to attack by the Pt-containing substance than normal cells as a consequence of the higher permeability of the former to low-molecular weight Pt species formed in vivo, as well as to the high-dose, short-term conditions of administration (sort of acute exposure) which leave healthy cells practically unaffected. This situation may dramatically change as the permanent presence of much lower concentrations of Pt in the environment completely switches the scenario to that of chronic exposure, the impact of which on the healthy cells of living organisms is partly unknown and partly worrisome (e.g. the increase in mutagenic events of health care personnel manipulating Pt-containing drugs) (Vaughan and Florence 1992). Other uses of Pt-group elements

Table 1 Result of the quality control analysis

	PGMs	Standard. conc. Sarm7	Results obtained after NAA analysis of the standards.			Mean	% Recovery
			Std. 1	Std. 2	Std. 3		
	Pt/ $\mu\text{g/g}$	3.74	3.67	3.71	3.71	3.69	98.6
	Pd/ $\mu\text{g/g}$	1.53	1.49	1.50	1.50	1.50	98.0
	Rh/ $\mu\text{g/g}$	0.24	0.2371	0.2379	0.2378	0.2375	98.95

The above results suggest that the analytical method used was very reliable

(jewelry) in industry and dentistry may also contribute to their availability in the biosphere and hence to the global exposure to humans through both inhalation and diet (Hoppe 1965).

In the context given above and given the still keen lack of much reliable experimental data on the levels of Pd, Pt and Rh in water and sediment in Ghana, this study determined the concentration of such elements in the water and sediment of the Pra estuary in the Western Region of Ghana where it is estimated that more than two thousand cars passes over the bridge under which the river flows to join the sea each day.

The chemistry of platinum group compounds in aqueous solutions is dominated by their complex compounds. Many of the PGM salts, particularly, those with halogen- or nitrogen-donor ligands, are water soluble. Platinum (as well as the other platinum group metals) has a pronounced tendency to react well with carbon compounds, (Barefoot 1997), such as alkenes and alkynes, forming Pt^{II} coordination complexes. Oxidized platinum can lead to the formation of platinum^{IV} compounds.

Platinum in it highest oxidation state, Pt^{VI} is a strong oxidizing agent (Tohs and Bagchi 1995; Nriagu 1990). The Pt^{II} and Pt^{IV} states are the most stable. Although the metal does not corrode in air at any temperature, it can be affected mostly by halogens, cyanides, sulfur and other heavy metals and hydroxides. It seems that in an aquatic environment, organic matter in the form of humic and fluvic acids bind many heavy metals including PGMs. In soils, the mobility of platinum (PGMs) depends on

Table 2 Mean concentration of PGMs and pH in river bank sediment of all the four sampling sites

Sample	Pt/ $\mu\text{g/g}$	Pd/ $\mu\text{g/g}$	Rh/ $\mu\text{g/g}$	pH
A1	0.141±0.0211	0.311±0.096	0.008±0.00121	7.24
A7	0.158±0.041	nd	0.035±0.00523	7.13
B1	0.027±0.00397	0.016±0.0024	0.036±0.0054	6.91
C1	0.017±0.0025	nd	0.023±0.0034	6.51
DI	nd	nd	0.046±0.0069	6.45

A1 Sediment taken from river bank right hand side from C/C – Takoradi at Beposo, A7 Sediment taken from river bank left hand side from C/C – Takoradi at Beposo, B1 Sediment taken from river bank at Bosomdo next village from Beposo, C1 Sediment taken from river bank at Krobo, DI Sediment taken from river bank at Shama Beach

Table 3 Mean concentration of PGMs and pH in sediment three meters away from the river bank of all the four sampling sites

Sample	Pt/ $\mu\text{g/g}$	Pd/ $\mu\text{g/g}$	Rh/ $\mu\text{g/g}$	pH
A2	0.0636±0.0163	0.232±0.035	0.0186±0.0028	8.29
A3	0.0246±0.0063	0.046±0.0069	0.055±0.0083	8.14
A4	0.059±0.0089	0.120±0.0181	0.0404±0.0061	8.24
A5	0.017±0.0026	0.0405± 0.0061	0.0109±0.0015	8.29
A8	0.1003±0.0263	0.307±0.0461	0.0325±0.0047	8.13
A9	0.189±0.0284	0.537±0.081	0.047±0.007	5.25
A10	0.0031± 0.00048	0.0491± 0.0074	0.0269±0.0045	6.87
A11	0.119±0.0221	0.447±0.067	0.035±0.0053	5.91
A12	nd	0.395±0.059	nd	6.61
B2	0.0637± 0.0176	0.217±0.033	0.0380±0.0057	6.94
C2	0.0795±0.0213	0.0165± 0.0173	0.0147±0.0021	6.94
D2	nd	0.1932± 0.0288	0.0436±0.0066	6.56

A2 Sediment three meters away from A1, A3 Sediment three meters away opposite side of A1, A4 Sediment three meters away between old and new bridge, A5 Sediment on the old bridge, A8 Sediment three meters away from A7, A9 Sediment on new bridge away from Beposo town, A10 Sediment beside A9, A11 Sediment on new bridge near Beposo town, A12 Sediment under old bridge, B2 Sediment three meters away from B1, C2 Sediment three meters away from C1, D2 Sediment three meters away from D1

the pH and redox potential, chloride concentration of water, and the chemical form of Pt (PGMs) in primary rocks. It is considered that Pt (PGMs) will be mobile in acidic soil with high chloride content. These soil conditions increases the availability of Pt and other

Table 4 Mean concentration of PGMs and pH in waterbed of all the four sampling sites

Sample	Pt/ $\mu\text{g/g}$	Pd/ $\mu\text{g/g}$	Rh/ $\mu\text{g/g}$	pH
A6	0.0468± 0.0070	0.0052±0.0008	0.0126±0.002	6.69
B5	0.0503± 0.0185	nd	0.0054±0.0008	6.55
C5	nd	0.1225±0.0183	0.0177±0.0027	6.52
D5	0.171± 0.0603	0.299±0.045	0.037±0.0056	6.40

A6 Waterbed at Beposo, B5 Waterbed at Bosomdo, C5 Waterbed at Krobo, D5 Waterbed at Shama Beach

Table 5 Mean concentration of PGMs and pH in water samples of all the four sampling sites

Sample	Pt/ $\mu\text{g/L}$	Pd/ $\mu\text{g/L}$	Rh/ $\mu\text{g/L}$	pH
AW	0.0095 \pm 0.0025	0.0105 \pm 0.0036	0.0013 \pm 0.00019	7.58
BW	0.0032 \pm 0.0009	0.032 \pm 0.005	0.0034 \pm 0.0005	7.52
CW	nd	0.0373 \pm 0.0028	0.0067 \pm 0.00101	7.58
DW	0.0065 \pm 0.0017	nd	0.0022 \pm 0.0003	7.07

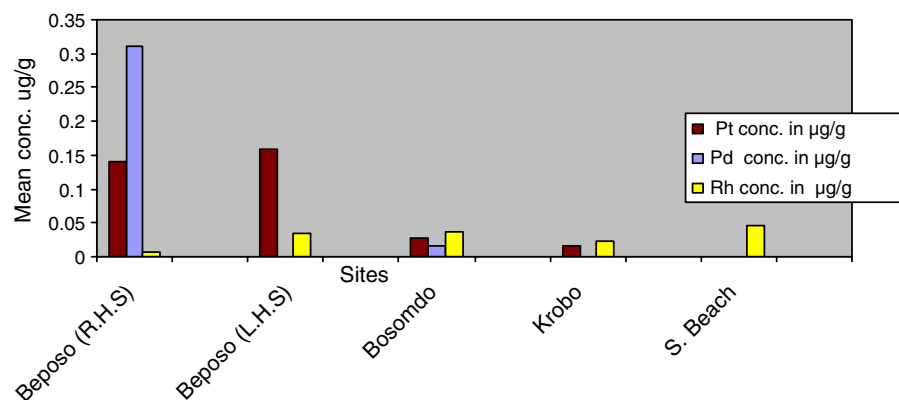
AW Water sample taken from Biposo, *BW* Water sample taken from Bosomdo, *CW* Water sample taken from Krobo, *DW* Water sample taken from Shama Beach

PGMs to plants. This is essential because it suggest that platinum (PGMs) emitted into the environment can form soluble substances that are absorbed by plants, raising the possibility of its presence in the food chain.

Materials and methods

Sample collection

The water samples were collected in a camera film container of about 10 mL capacity and stored in an ice chest to the laboratory. In the laboratory the samples were stored in a deep freezer for further analysis to be carried out. Water samples were collected from various sites starting from Beposo, Bosomdo, Krobo and Shama Beach along the bank of the Pra River. This was done four times at two weeks intervals.

Fig. 3 A plot of PGMs mean concentration in river bank sediment versus collection sites

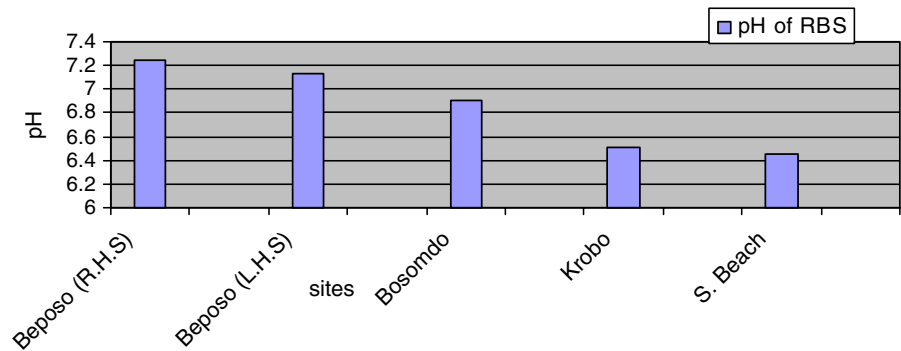
Improvise dedicated plastic scoop was used for sediment sampling where about 50 g of sediment were scooped into film container. Samples were taking from water bed, water bank and three meters from water bank at Beposo, Bosomdo, Krobo and Shama Beach. At Beposo samples were also taken from the bridge and it environ as indicated in the map (Fig. 2). Control samples (water, sediment and water bed) were also taken from non vehicular activity and were further prepared for laboratory analysis by air drying. The maps (Figs. 1 and 2) show the sampling sites.

Sample preparation and analysis

Calibrated Eppendorf tip ejector pipette was used to pipette 0.5 mL of each water sample into clean pre-weighed 1.5 mL, rabbit capsule and reweighed and heat-sealed using soldering rod. Four of these sample vials were placed into a 7.0 mL volume rabbit capsule and also heat-sealed. Two replicates were prepared for each sample.

Each sediment sample was air-dried for three days in a clean environment. Other organic debris and particles such as shells, stones, and micro-organisms were hand picked from the samples. The samples were crushed using an agate mortar and pestle, sieved using an 85 μm mesh size USA standard sieve (Fisher Scientific Co., USA) and homogenised. About 100 mg of each sample was weighed into a clean polyethylene film. The films were wrapped and heat-sealed. These samples were labelled according to their site. Two replicate sub-samples were prepared for each sample. The samples were packed into 7 mL volume rabbit capsules for irradiation.

Fig. 4 A plot of river bank sediments (RBS) pH versus collection sites



Irradiation of sample and counting

Each of the samples was sent by the pneumatic transfer system into the Am-Be source for irradiation. In this regard, one hour was chosen for all the samples because all the metals in question were all medium lived. These samples were irradiated for one hour and left overnight for cooling or decaying process to take place. The samples were then counted the next day for 600 s and their intensities saved for further analysis.

Data processing

The detector type used for the counting of signals was the ENERTEC High Germanium (HPGe) detector of 3000 (+ve) bias and a resolution of 2.55keV for 1332KeV photo peak of Co-60. The signals from the detector were passed through the spectroscopy amplifier, and then accumulated by the Canberra Multi-Channel Analyzer (MCA) for a present time. The spectra from the MCA were transferred to a DEC 350 microcomputer for analysis using Gamma spectrum analysis software (*Ortec multi-channel buffer (MCB)*). This software identifies the various photo peaks and

works out the areas under them. By means of radioactive decay law (Tolgyessy and Kyr 1989), the concentration of each element was calculated.

Validation of method

Validation of the analytical procedure was undertaken by measuring three each 101.2 mg of Reference material IAEA-405 (NIM SARM 7) – trace and major elements in estuarine sediment and 104.4mg IAEA-1646a (NIM SARM 9) – estuarine sediment provided by US Department of comm. National Inst. of standards and tech. Gnitherbury, MD 20899 (certified standard for Pt, Pd and Rh) and irradiated and counted under identical experimental conditions.

Determination of pH of soil samples

For the pH, 1.00 g of dried soil samples of each soil sample was weighed and dissolved in 100 mL of distilled water for 24 h. The supernated solution was filtered to get a clear solution and the pH of the subsequent solution was determined using the pH meter.

Fig. 5 A plot of PGMs mean concentration in sediments versus collection sites

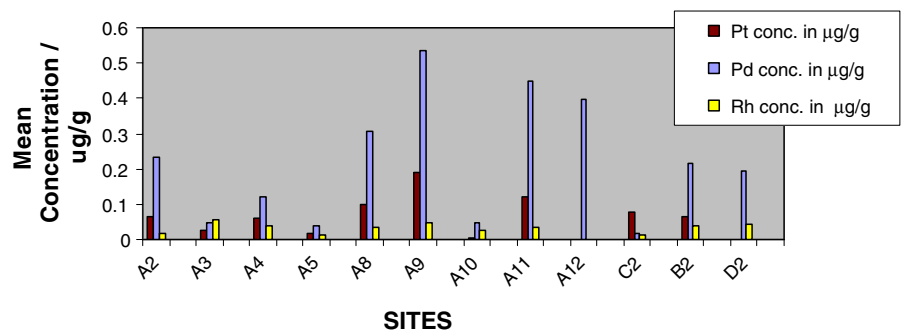
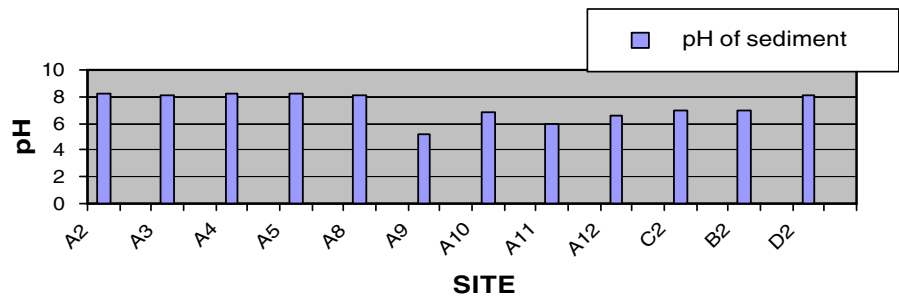


Fig. 6 A plot of sediments pH versus collection sites



Determination of pH of the water samples

The frozen water samples were allowed to attain the normal room temperature of about 26°C. The pHs of the water samples were determined with a pH meter.

Results and discussion

The performance of the analytical method: Reliability criteria and validation is reported in Table 1. The values of merit for PGE determination by neutron activation analysis (NAA) in a certified reference material (NIM, SARM 7 and SARM 9), which, however, has a certified values of 3.7, 1.53 and 0.24 $\mu\text{g/g}$ of platinum, palladium and rhodium respectively. The detection power offered by the technique in the investigated matrices was checked by analyzing two each of independent samples of NIM, SARM 7, SARM 9 standard reference materials.

One reference material was used as standard in the analysis using excel program and the rest of the standard (std) materials were run along side with the samples, just as was done for the samples.

The same procedure was used to calculate the limits of quantification (LoQs) and, the reporting limits (equal to or higher than the LoQs). The reproducibility was assessed by calculating the RSD (%) of measurements performed on

five independent aliquots in the same analytical run. The instrumental precision was evaluated and monitored over the entire working range by performing replicate analyses of the standards.

As regards the test for accuracy, unfortunately, no certified reference materials for PGMs in the said matrices are commercially available. Consequently, reliability of measurements was checked through recovery tests by using standard reference material SARM 7 and SARM 9 as standard concentration, 1 and standards 2 and 3, in the analytical runs as a set of four independent samples. Standard 4 was used as the main reference material in the analysis.

Overview of PGM concentration in sediment and water

Tables 2, 3, 4, and 5 presents the average mean concentration levels of the metals examined during the dry and the raining season. From the tables it was observed that the concentration of the metals fluctuated between the four sampling site. Comparing the mean concentration of Pt, Pd, and Rh in the soil samples in Table 2, it could be realized that, the river bank sediments from Beposo (marked as A1 and A7) had high accumulation level of all the metals studied which was followed by Bosomdo and Shama Beach.

Fig. 7 A plot of PGMs mean concentration in waterbed versus collection sites

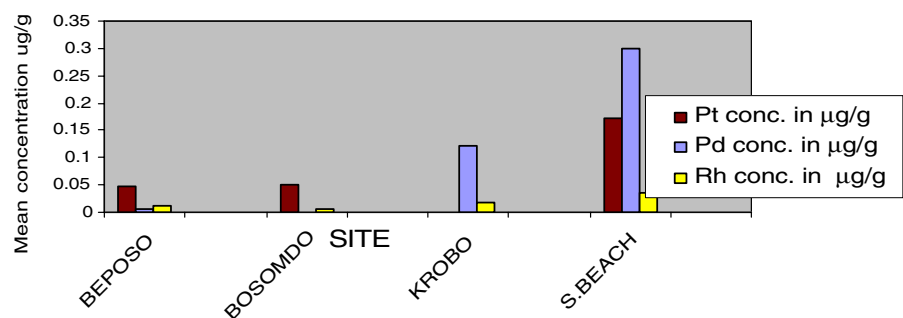
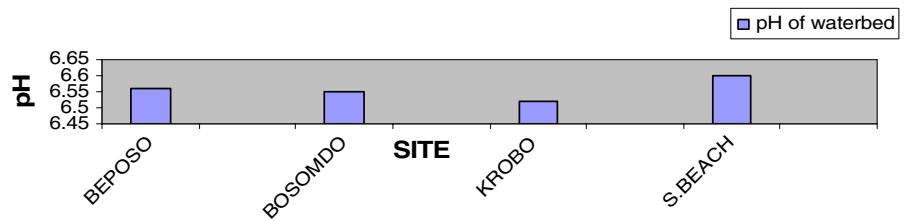


Fig. 8 A plot of waterbed pH versus collection sites



The high concentration at Beposo could be attributed to the high traffic density on the bridge where these cars ply everyday. This was seen in the sediments taken from the bridges (both new and old) which gave the highest concentration of 0.003–0.189, 0.049–0.537, and 0.0269–0.047 $\mu\text{g/g}$ of Pt, Pd, and Rh respectively in Table 3. This similar observation was made by Essumang et al. (2006) in their study of vehicular fallout in the Kumasi metropolis of Ghana. In all the metals analyzed, palladium was found to be the most abundant metal for the entire site studied with an average mean value of 0.049–0.537 $\mu\text{g/g}$ followed by Pt with the average mean concentration of 0.003–0.189 $\mu\text{g/g}$. The higher Pd emission is as a result of the fact that, Pd portion in the catalytic converter has increased in recent years to about 96% as it seeks to substitute the dominant use of Pt in the converter (Lustig et al. 1997).

In Figs. 3 and 4, 5 and 6, 9 and 10, it could be seen that the concentrations decreased with high acidity (low pH) and increased with low acidity (high pH) or in alkaline medium. This can be explained that, acidity enhances solubility and mobility meaning that most of the metals in this condition would be soluble and be taken up by plants, animals and may form other type of compounds as well. Also, at acidic medium metals are highly mobile which means they are easily washed down stream so fast and that could be the reason why the concentration decreases. In the case of alkaline condition, on the other hand, it may make some minerals or metals so insoluble that they cannot be taken up in solution by the plant, animal or forming other compounds, hence, could be accumu-

lated as shown in the result in the mean tables above. The trend is the opposite for Figs. 7 and 8 which were the concentrations found in the waterbed from all the sites. This can be explained that, at Beposo where the metals are believed to be emitted into the environment by automobiles, metals are washed down stream because of fast tidal wave of the water. This means that most of the metals are washed downstream to Shama Beach where the fresh water meets the sea.

At the Shama Beach site, accumulation was found to be high as shown in Table 4 or Fig. 7, where high mean concentration of 0.299, 0.171, and 0.037 $\mu\text{g/g}$ of Pd, Pt, and Rh respectively were recorded. This can be explained that the tidal wave speed becomes barely low as the two extreme forces meets and the metals which were carried from upstream then get deposited in the waterbed. That is, at Beposo trace amount are likely to be deposited in the waterbed which accounted for small amount in the waterbed concentration values recorded there (A6) in Table 4 or Fig. 7.

Comparing the results of the water samples taking from all the four sites in Table 5, it could be seen that high concentration of Pd were found at Bosomdo and Krobo villages. These villages are about 2.0 and 1.5 km from Shama Beach respectively and also 1.0 and 1.5 km from Beposo respectively. These were followed by Beposo with Shama Beach recording concentration below detection limit between of 10 ppb for Pt and Pd and 100 ppb for Rh.

This can be explained that sampling was taken first during the dry season where most of the metals have been washed down stream with less amount of water, concentration were expected to be high at these areas.

Fig. 9 A plot of mean concentration of PGMs in water versus collection sites

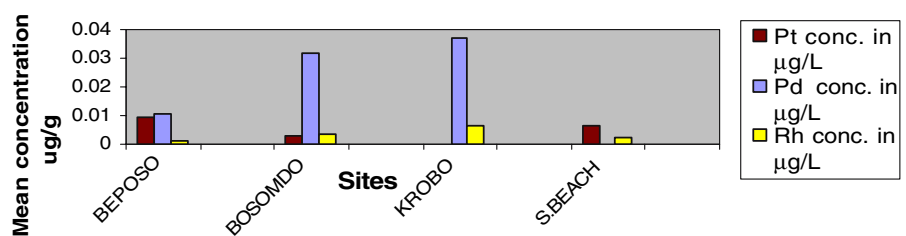


Table 6 Control sample taking from non vehicular activity site (Akotokyir Kakum Estuary) and pH

Sample	Pt/ $\mu\text{g/L}$	Pd/ $\mu\text{g/L}$	Rh/ $\mu\text{g/L}$	pH
EW	nd	nd	nd	7.02
E2	nd	nd	nd	6.59
E3	nd	nd	nd	7.40

EW Water sample taken from Akotokyir Kakum Estuary (non-vehicular activity site), E2 Sediment taken from river bank at Akotokyir Kakum Estuary, E3 Sediment three meters away from E1

As time went on (at the peak of the raining season more water entered the estuary) the concentration of the metals decreased drastically in all the four areas studied. Most of the metals would have been washed downstream by high tidal wave at Beposo and as it approaches Bosomdo and Krobo it become steady and most metals will settle depending on the acidic nature of the water. It can also be stated that at Krobo, alkalinity nature also may lead to high concentration of metals as demonstrated in Fig. 9. The concentration below detection limit obtained at Shama Beach can be as a result of high acidic conditions.

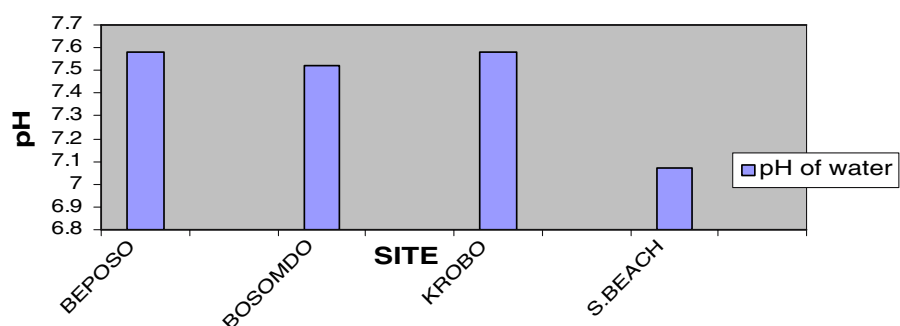
The concentration obtained for this research recorded an increase in the concentration (0.001–0.44 $\mu\text{g/g}$) of PGMs in the sediment samples from the river banks, waterbed, and sediment three meters away from the river bank and water samples. The reason could be that most of the metals emitted by the automobile were being washed into streams, estuary, sea etc. hence its accumulation in these sites. The result compared to mean UK dietary intake were found to be below those values (Ysart et al. 1999). Though they showed very low levels which might not pose danger to human health, however, they are bioaccumulative and that calls for concern.

Toxicological studies have shown that gastrointestinal absorption of Pt salts is extremely low (<5% of oral dose). Excretion of most of the absorbed fraction is normally via the faeces. The acute toxicity of Pt salts is dependent on water solubility (the more soluble salts being more toxic) and speciation. Few useful animal toxicity data of Pd are available. After a single dose of ^{103}Pd (as $^{103}\text{PdCl}_2$) in rats, absorption was poor, only 0.5% of dose being excreted subsequently in urine. Repeated dose toxicity studies have shown that some soluble Pt salts are mutagenic in vitro as well as being generally cytotoxic. In animal and or humans *cis*-platin has been reported to show myelotoxicity, nephrotoxicity and ototoxicity (CPMP/SWP/QWP 2002). No occupational poisoning has been shown via the inhalation or dermal routes. Rhodium oral uptake is reported to be very low. Simple Rh compounds such as RhCl_3 have been reported as genotoxic and others are cytotoxic. Studies show that Rh compounds appear to be less toxic than their Pt counterparts (CPMP/SWP/QWP 2002).

Table 6 present mean concentrations of control samples taken from non vehicular activity site (Akotokyir Kakum Estuary) which showed concentrations below detection limit of 10 ppb for Pt and Pd and 100 ppb for Rh were recorded which far lower than those high vehicular activity areas which are shown in Tables 2 to 4 above.

This strongly suggests that vehicular activities are contributing to the release of PGMs into our environment. As a result, pragmatic efforts should be made to prevent individuals from been exposed to high concentrations of these metals in the environment.

Pra estuary is the major source of drinking water to western region and some parts of central region. Water is pumped from the river, treated and distributed to homes and businesses on the Sekendi/

Fig. 10 A plot of water pH versus collection sites

Takoradi water system. The villages situated along the river use the water directly for drinking, cooking and washing. However, it is very necessary to know the extent of pollution from time to time.

The major activities along the banks of the river include intensive farming of which the main crops produce are plantain, banana, cassava and other tuber crops and fishing. Also, the river is used by the inhabitants as a means of transport.

Conclusion

By applying modern analytical method, Neutron Activation Analysis (NAA) in the determination of PGMs in the Pra estuary and its environment, an appreciable amount of Pd, Pt and Rh were detected. The highest concentrations (0.537 ± 0.081 $\mu\text{g/g}$ of Pd and 0.189 ± 0.0284 $\mu\text{g/g}$ for Pt) were found on the bridge (old and new) and its immediate environs which lies across the Pra estuary. This decreased down to Bosomdo and Krobo while increasing at Shama Beach (no vehicular Activity) where the estuary meets the sea. The availability of Pd and Pt should be of great concern as there are known mutagenic and toxic effect, even at exceedingly low concentrations in urban water (affecting ecosystem. Again, suspected biomethylation of Platinum in the aquatic urban environment gives a similar concern as that of mercury (CORDIS 2003). The results have also shown that, high concentration of acidity increased the solubility and mobility of these metals in both the water bodies and soil, and this may have tendency of entering the food chain (Fig. 10).

The result of the study has established that vehicular activities on the Cape Coast – Takoradi highway may have resulted in the elevated levels of PGMs in the soil and water bodies along the road. These PGMs were subsequently washed into the Pra estuary by runoff. Finally, Pd was found to have the highest concentration in almost all the samples analyzed for in this research which establishes the fact that Pd use in catalytic converters seems to be increasing.

Once again, it is clear from the results that the inhabitants of Beposo and its surrounding areas who use the estuary for farming and drinking are at risk of exposure to Pt, Pd, and Rh. Even though the levels obtained were below the mean permissible levels it still dangerous as these metals bioaccumulate. Prag-

matic measures should be taken to prevent individuals from being exposed to high concentrations of these metals in the environment. With this and many other problems with PGMs it is important that regular monitoring is done to ensure good health for all.

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References

- Barbante, C., Veysseyre, A., Ferrari, C., Van de Velde, K., Morel, C., Capodaglio, G. et al. (2001). Greenland Snow evidence of large scale contamination for platinum, palladium, and rhodium. *Environmental Science & Technology*, *35*, 835–839.
- Barefoot, R. (1997). Determination of platinum at trace levels in environmental and biological materials. *Environmental Science & Technology*, *31*, 309–313.
- CORDIS (2003). Assessment of environmental contamination risk by platinum, rhodium and palladium from automobile catalyst. Environment and Climate. http://cordis.europa.eu/data/PROJ_ENV/ACTIONeqDndSESSIO Neq27617200595ndDOCeql7ndTBLeqEN_PROJ.htm.
- CPMP/SWP/QWP (2002). The European Agency for the evaluation of medicinal products. Evaluation of Medicines for Human use. London, 17 December 2002, CPMP/SWP/QWP/44446/00. Corrigendum to the version dated 26th June 2002.
- Dominici, C., Petrucci, F., Caroli, S., Alimonti, A., Clerico, A., & Castello, M. (1989). A pharmacokinetic study of high dose continuous infusion cis-platin in children with solid tumors. *Journal of Clinical Oncology*, *7*, 100.
- EPA (2000). United States Environmental Protection Agency Washington, D.C. 20460. Office of Air and Radiation. <http://www.epa.gov/otaq/cert/factshts/catcvrts.pdf>.
- Essumang, D. K., Dodoo, D. K., Obiri, S., & Oduro, B. A. K. (2006). Analysis of vehicular fallouts from traffic in the Kumasi metropolis. *Bulletin of the Chemical Society of Ethiopia*, *20*(1), 9–15.
- Ensslin, A. S., Pethran, A., Schierl, R., & Fruhmann, G. (1994). Urinary platinum in hospital personnel occupationally exposed to platinum-containing antineoplastic drugs. *International Archives of Occupational and Environmental Health*, *65*, 339–342.
- Helmers, E., Mergel, N., & Barchet, R. (1994). Platin in Klärschlammasche und an Gräsern UWSF-Z. *Umweltchem. Ekotox*, *6*(3), 130–134.
- Hodge, V. F., & Stallard, M. O. (1986). Platinum and palladium in roadside dust. *Environmental Science & Technology*, *20*Ž, 1058.
- Hoppe, R. (1965). Chemistry of the noble gases. *Fortschritte der chemischen Forschung*, *5*, 213–346.

- IPCS (International Programme on Chemical Safety) (1991). *Environmental health criteria 125: platinum*. Geneva, Switzerland: World Health Organization Press.
- Känig, H. P., Hertel, R. F., Koch, W., & Rosner, G. (1992). Determination of platinum emissions from a three-way catalyst equipped gasoline engine. *Atmospheric Environment A*, 26, 741.
- Lustig, S., Schierl, R., Alt, F., Helmers, E., & Kümmerer, K. (1997). Schwerpunktthema: platin in Umweltkompartimenten-Deposition, Verteilung sowie Bedeutung für den Munched und sein Nahrungsnetz. UWSF- Z. Umweltchem. Ökotox, 9, 149–152.
- Nriagu, J. O. (1990). Heavy metal pollution poisoning the biosphere. *Environment*, 32(7), 7–11.
- Nriagu, J. O., & Pacyna, J. M. (1988). Quantitative Assessment of world wide contamination of air, water and soil by trace metals. *Nature*, 333, 134–139.
- Ranch, S., Motelica-Heino, M., Morrison, G., & Donard, F. (2000). Critical assessment of platinum group element determination in road and urban sediment using ultrasonic nebulization and high resolution ICP-MS. *Journal of Analytical Atomic Spectrometry*, 15, 329–334.
- Rosner, G., & Merget, R. (1990). Allergenic potential of platinum compounds. In A. D. Dayan, R. F. Hertel, E. Heseltine, G. Kazantzis, E. M. Smith, & M. T. Van der Venne (Eds.) *Immunotoxicity of metals and immunotoxicology* (pp. 93–100). New York, London: Plenum.
- Siva, S. N., Masuda, A., & Hirata, T. (1990). LA – ICP – Mass Analysis of Platinum in Environmental Soil Samples Following Micro – Fire Assay Technique in Symposium on Mass Spectrometry, 8th ISMAS, Hyderabad, India, Proceedings Volume, p. 535–537.
- Tohs, S. J., & Bagchi, D. (1995). Oxidative mechanisms in the toxicity of metal ions. *Free Radical Biology & Medicine*, 18, 321–336.
- Tolgyessy, J., & Kyrs, M. (1989). *Radio analytical chemistry* (Vols 1 and 2., pp. 1–354). Chichester: Ellis Horwood Ltd.
- U.S. Commercial Service (2006). Your Global Business Partner <http://www.buyusainfo.net>
- Vaughan, G. T., & Florence, T. M. (1992). Platinum in the human diet, blood, hair and excreta. *Science of the Total Environment*, 111, 47.
- Ysart, G., et al. (1999). Dietary Exposure estimates of 30 elements in the UK Total Diet Study. *Food Additives and Contaminants*, 16(9), 391–403.