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Distribution of Lead in Kerbside Soils

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ABSTRACT

Lead in emissions from motor vehicles using leaded petrol are usually monitored by analysing gas samples. In view of the many problems associated with gas sampling, this project focussed on the analysis of lead in kerbside samples. To this end, soil samples were collected from kerbsides and road islands within and outside the city of Durban. Thus urban, peri-urban and rural roads were included in the survey. In a preliminary study, kerb-side dust samples were collected from a vehicle-busy city street where many pavement food vendors ply their trade. The horizontal distribution of metals as a function of distance from the kerb was determined by analysing samples which were collected at various distances of 1–20 metres from the edge of a road. The determination of vertical distribution of lead was achieved by taking samples at depths of 0–2 cm, 10–15 cm and 20–25 cm at each of the sampling spots. Some sub-samples were leached at pHs found in soils using a Hazardous Waste Filtration System while parallel sub-samples from the same gross sample were acid-digested in a Microwave Digester. Analyses were done using ICP-AES, AAS and GF-AAS. The values for lead were found to be highest for urban sites and lowest for rural ones. Values of lead from leached samples were found to be lower than that for digested samples whilst the values for lead over all sites was in the range 0.02–923 ppm.

KEYWORDS

Lead, soils, kerbside, distribution, analysis.

1. Introduction

Kerbside soils are subjected to pollution from various sources depending on the level of industrialization of a country and waste dumping practices. Motor vehicle emission is one of the main sources of kerbside pollution in developed areas of South Africa. Leaded petrol was used on a large scale at the time this study was being carried out.

The toxicity of lead to humans has been well documented.[1] In areas subjected to heavy and slow-moving vehicular traffic, the amount of lead exhausted may be quite high.[2] Since exhaust fumes settle on kerbsides, soil samples from these areas may give a good measure of the accumulation of lead. This approach eliminates the need to risk expensive sampling equipment needed for collecting air samples. However, this method of assessing the extent of the pollution of kerbsides by vehicular emissions is fraught with problems. Among the challenges in using kerbside soils as indicators of metal pollution, are the natural abundances of metals in soils and that due to the disposal of domestic waste such as building rubble. In this project these challenges have been met by using variety of sampling strategies.

Furthermore, it is not simply sufficient to know how much motor vehicle emissions contribute to kerbside pollution. It is equally important to ascertain the availability of the metals in the soil, that is, it is of great interest to know the extent to which the metals can be retained by the soil or leached from it by groundwater. This paper addresses this and other issues mentioned above.

2. Experimental

2.1. Materials Used

Nitric acid (90% Analar Grade) was purchased from Reidel de Haen and used as received. Standard solution of lead (1000 ppm) was obtained from SaarChem and diluted as required by the serial method using purified water (18 s mol^{-1}). Nitrogen (>than 99.99% pure), compressed air (>99.99% pure) and argon (>99.99% pure) were obtained from Afrox. Millipore fibreglass pre-filters (124 mm diameter) and hardened filter papers (Whatman 142) medium speed were used in filtrations involving the Millipore Hazardous Waste Filtration System. Buffer solutions (phosphate) of pH 4 and pH 7 were purchased from BDH Laboratory. Certified Reference Material (NCS DC 73320) for soil was obtained from Industrial Analytical. Double deionised water, which was used in all preparations of solutions, was obtained from a Milli-Q Water System located in the laboratory.

2.2. Sampling Sites and Sampling

Urban (city of Durban), peri-urban and rural sites were sampled. The first sample at each spot was taken at a depth of 0-2 cm with a hard plastic spatula and placed in polythene bags. Along the kerb, the distance between sampling spots was about 20 m. Distances from the kerbside were either 1, 2, 4, 8 and 12 m or 2, 10, 20 and 30 m depending on terrain and/or rockiness of the ground. For depth variation, samples were collected from each spot at distances of 0–2 cm, 10–15 cm and 20–25 cm from the surface using a stainless steel corer. Samples were also collected on traffic islands between dual roads.

Samples were collected from sites labelled A–E. Site (A), was a pavement of a street near a market and bus rank (Victoria Street Bus Rank). Site (B) comprised road islands opposite a school and a University of Technology (Centenary Road) and represented an inner city area. Site (C) was a recreational area (Botanical Gardens). Site (D), a peri-urban traffic intersection (Umgeni/Goble) on the outskirts of the city while site (E) was a rural location along a highway (N2, Shongweni).

2.3. Sample Treatment and Sample Preparation

Each bulk sample, of mass 1–2 kg, was dried in an oven at 105°C

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for 48 hours, cooled in a desiccator and then sieved through King Test 2.00 mm and 425 μm stainless steel sieves. The fine material was thoroughly mixed by shaking the soil in a clean plastic box. The samples were stored in clean plastic bags at room temperature.

For digestion purposes sub-samples (about 1 g) were weighed into acid-washed teflon vessels of a Milestone High Performance Microwave Digestion Unit. Nitric acid (2 mL of 70% Analar Grade, Riedel-de Haen) was added to each vessel.[3–6] The digestion was done in three steps of five minutes each. The power was 250 W, 400 W and 500 W, respectively, for the three stages. After cooling, the digests were quantitatively transferred to acid-washed beakers and filtered through a Millipore Corporation Hazardous Waste Filtration System equipped with a fibreglass pre-filter and Whatman medium-speed filter into 250 mL plastic volumetric flasks and volume made up with double deionized Milli-Q water. The filters were pre-cleaned by washing with nitric acid (1 M) and double deionised Milli-Q water.

In the leaching experiments, soil samples (100.0 g portions) were weighed into 800 mL acid-washed beakers. Double deionised water (500.0 mL) adjusted to pH 4 was added together with a magnetic stir-bar. The beaker was sealed with parafilm (Shalom Laboratory) and the suspension was stirred for 24 hours in an air-conditioned laboratory (23°C). The resulting mixture was filtered using a Millipore Corporation Hazardous Waste Filtration System as described above. The volume of the final solution was 500.0 mL.

2.4. Calibration of AAS, ICP-AES and GF-AAS

A multi-point calibration was used to optimize and calibrate the Varian AA-1275 Atomic Absorption Spectrometer. A blank and five standard solutions of lead were prepared from 1000 ppm standard by serial dilution. An average of three replicate values of absorbance per standard solution was taken. The calibration line obtained by plotting the data obtained. The same procedure was used for the other two instruments except that the calibration ranges were different. In all cases the calibration range was such that the interpolation method could be used. All samples that had an absorbance value that was outside the range of values obtained by standard solutions were diluted accordingly in both leaching and digestion experiments. The concentration of the unknown was calculated using the equation for a straight line. The final result was obtained by multiplying the concentration of an unknown by a dilution factor. Furthermore, statistical tools were used to calculate the 95% confidence limits.

3. Results and Discussion

3.1. Preliminary Studies – Usage of Leaded and Unleaded Petrol

Since the study was concerned with the amount of lead exhausted from cars it was decided that a limited survey to ascertain the relative amounts of leaded and unleaded petrol purchased by motorists at six petrol stations located within the city of Durban should be conducted. It was found that the average per day for a period of four weeks was 88.9% for leaded petrol and 11.1% for unleaded petrol.

Table 1 Concentration (ppm) of Pb in the reference material.

Quoted concentration of Pb in CRM #NCS DC 73320	Concentration of Pb obtained by analysis	% Recovery
20.00 ± 4.00	18.99 ± 1.87	94.95

3.2. Validation of Methods

The validation of the method of sample digestion and analysis was done as follows: a comparable sample of a certified reference material (for soil), NCS DC 73320 supplied by Industrial Analytical (Pty) Ltd of South Africa and approved by the China National Centre for Iron and Steel was digested under identical conditions to that used for test samples. The resulting solutions were analysed using ICP-AES, as this was the technique used in the bulk of the analyses. The comparison of the results together with the recovery is given in Table 1.

3.3. Dust Samples from Site A (Main Bus Rank in Durban) and Soil Samples from Site B (Traffic Islands)

Dust samples were taken from five spots (at site A) separated by 8 m from one another. The bus rank is surrounded by roads that carry very high traffic volumes. Lead was found to range between 250.90 ± 20.12 and 115.63 ± 11.16 ppm in digested samples, and in the range 2.52 ± 0.26 and 2.12 ± 0.46 ppm in leached samples. Soil samples were collected from three spots on islands in the roadway in front of a University of Technology. The concentration of lead was found to be in the range 223–337 ppm (Table 2).

3.4. Soil Samples from Recreational Area (Botanical Gardens), Site C

Samples were collected from two spots at site C, namely the entrance to the Botanical Gardens (C1) and from approximately the centre of the Botanical Gardens (C2). Site C site is bounded by two roads which carry very heavy traffic, especially in the mornings and afternoons. The mean concentration of lead in the leached and digested samples, taken at the entrance to the site and at the centre of the site, were found to be 39.39 ± 0.88 and 93.23 ± 1.24 ppm, respectively, whereas the corresponding values for the spot at the centre were found to be 47.19 ± 3.87 and 88.69 ± 1.07 ppm (Table 3). As there is no great difference between the total concentration of lead in the sample from the entrance compared to that from the centre (approximately 200 m

Table 2 Concentration (ppm) of lead at site A.

	Digestion		Leaching	
Sample number	Mean of 3 at $P = 0.05$	RSD	Mean of 3 at $P = 0.05$	RSD
C1(entrance)	93.23 ± 1.24	0.54	39.39 ± 0.88	0.90
C2(center)	88.69 ± 1.07	0.49	47.19 ± 3.87	3.30
A1	183.14 ± 6.66	1.46	2.52 ± 0.26	36.13
A2	157.39 ± 13.67	3.50	2.12 ± 0.46	8.63
A3	209.49 ± 4.37	0.84	2.28 ± 0.22	3.87
A4	250.90 ± 20.12	3.23	2.29 ± 0.11	1.98
A5	115.63 ± 11.66	4.06	2.19 ± 0.24	4.44

Table 3 Concentration (ppm) of lead at site C.

	Digestion		Leaching	
Sample number	Mean of 3 at $P = 0.05$	RSD	Mean of 3 at $P = 0.05$	RSD
A1	183.14 ± 6.66	1.46	2.52 ± 0.26	36.13
A2	157.39 ± 13.67	3.50	2.12 ± 0.46	8.63
A3	209.49 ± 4.37	0.84	2.28 ± 0.22	3.87
A4	250.90 ± 20.12	3.23	2.29 ± 0.11	1.98
A5	115.63 ± 11.66	4.06	2.19 ± 0.24	4.44
C1 (entrance)	93.23 ± 1.24	0.54	39.39 ± 0.88	0.90
C2 (centre)	88.69 ± 1.07	0.49	47.19 ± 3.87	3.30

form the bounding roads) these results could be taken to show that the exhausted lead is carried for a considerable distance from the kerbside.

3.5. Soils samples from a Peri-urban Traffic Intersection, Site D (Umgeni/Goble Road Intersection)

Owing to hilly terrain, samples had to be collected from a sloping kerbside. The samples were collected at points which were 4.6 m, 10 m and 13 m from the edge of the roadway. To illustrate the effect of distance from kerbside on the concentration of the lead, a bar chart of concentration versus distance for leached and digested samples is given in Fig. 1. This figure shows that the concentration of lead increases with increasing distance from the road. This is contrary to the expectation that most of the emission will land fairly close to the kerbside. However, consideration of the terrain and air currents set up big vehicles suggests that emissions are lofted up before they land.

As expected, the values of lead concentrations of digested samples are generally higher than those for the leached samples. However, the relative closeness of the values for leached and digested samples appears to suggest that a relatively high percentage of the lead from the vehicles is exhausted as soluble species (Table 4).

3.6. Soil Samples from a Rural Site, E, Alongside a National Freeway

This site was chosen because it has large volume of free-flowing traffic. It is also flat, open (it allows for a collection of samples at varying distances from the kerb) and fairly undisturbed. Four sets of samples were taken at this site. The first set of samples was collected at 1, 2, 4, 8 and 12 m from the edge of the road. The results of lead obtained by leaching ranged from 8.73 ± 0.84–3.01 ± 0.39 ppm. Parallel portions of these samples were also digested and the concentration of lead was found to be high, ranging from 852.88 ± 7.11–189.05 ± 4.21 ppm. The results for the digested samples are depicted in Fig. 2. It is seen that the concentrations of lead decrease with distance from the kerb.

As part of horizontal sampling soil a second set was collected from spots 20 metres apart along the kerbside (Table 5a). For each spot samples were also collected at distances of 2, 4, 8 and 12 m

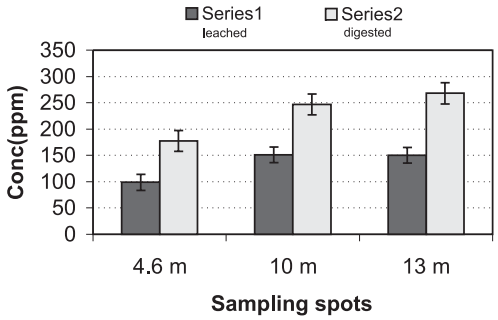

Figure 1 Variation of concentration of Pb with distance from the kerbside at a peri-urban site.

from the kerbside so as to provide 'grid sampling'.

To assess the effect of rain, on the concentrations of lead in the soil, a third set of samples was collected from the same site from both sides of the freeway after three days of heavy rains. The sampling spots were at 2, 10, 20 and 30 m from both sides of the freeway. The lead results were found to range from 0.065 ± 0.003–0.025 ± 0.002 ppm (Fig. 3). There was no significant difference in the concentrations of the corresponding samples from the two sides of the road.

To investigate the extent of seepage of metals,[7] a fourth set of soil samples was taken at varying depths from the surface. The sampling was carried out at five spots 20 m apart and 1 m from

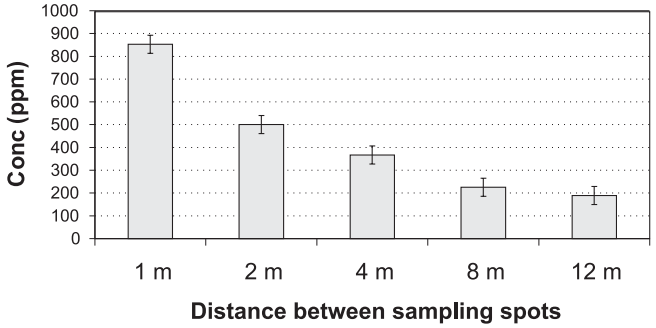

Figure 2 Pb results on digested samples from the rural roadside analysed by ICP-AES.

Table 4 Concentration (ppm) of lead at site D (a peri-urban site).

	Digestion		Leaching	
Sample number	Mean of 3 at $P = 0.05$	RSD	Mean of 3 at $P = 0.05$	RSD
4.6 m	177.59 ± 1.40	0.77	98.77 ± 5.03	1.64
10 m	247.03 ± 2.52	1.24	150.92 ± 2.80	1.08
13 m	268.00 ± 2.60	0.98	150.06 ± 2.46	1.22

Table 5 **(a)** Concentration (ppm) of lead for horizontal distribution at site E.

	Digestion		Leaching	
Sample number	Mean of 3 at $P = 0.05$	RSD	Mean of 3 at $P = 0.05$	RSD
1 m	923.31 ± 81.11	3.54	4.97 ± 0.53	4.31
2 m	674.99 ± 20.60	1.23	3.44 ± 0.46	5.36
4 m	193.36 ± 21.41	4.46	4.18 ± 0.18	1.69
8 m	171.89 ± 3.92	0.92	3.67 ± 0.17	1.84
12 m	162.71 ± 8.46	2.09	3.76 ± 0.27	2.90

(b) Concentration (ppm) of lead for vertical distribution at site E.

	Digestion		Leaching	
Sample number	Mean of 3 at $P = 0.05$	RSD	Mean of 3 at $P = 0.05$	RSD
0–2 cm	1449.10 ± 46.49	1.29	8.78 ± 0.63	2.87
10–15 cm	294.93 ± 17.77	2.43	5.21 ± 0.51	3.96
20–25 cm	26.18 ± 5.61	8.62	5.09 ± 0.37	2.89

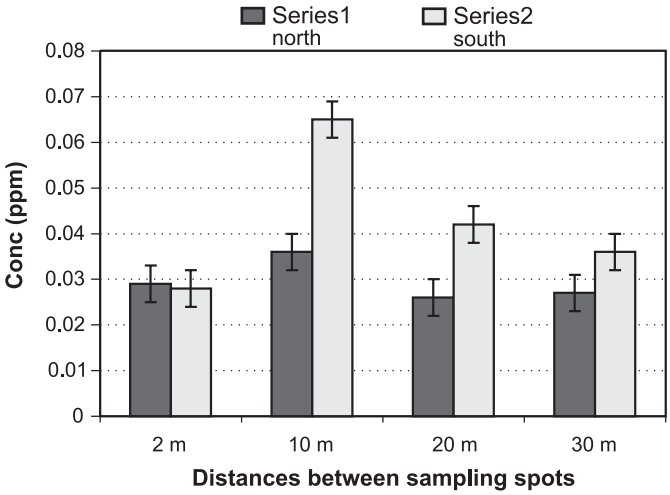

Figure 3 Pb results on leached samples from the rural roadside analysed by GF-AAS.

the edge of the road. Depths of 1–2 cm, 10–15 cm and 20–25 cm were used.

The concentration of lead in samples that were collected from 0–2 cm, 10–15 cm and 20–25 cm deep showed a decreasing trend with increasing depth (Fig. 4). However, there were no significant differences between the lead concentrations of the samples that were collected at depths of 10–15 cm and 20–25 cm (Table 5b).

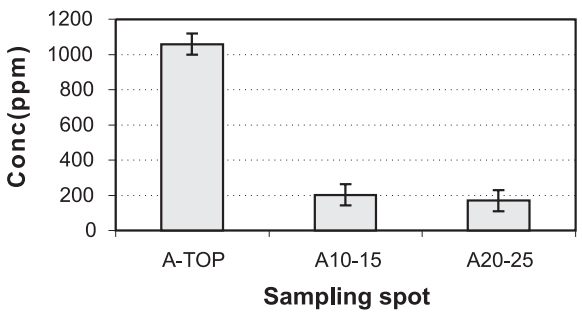

Figure 4 Pb result on digested samples analysed by ICP-AES showing the vertical distribution.

4. Conclusions and Recommendations

In assessing the information gleaned from this project, it should be borne in mind that this study was done against a backdrop of another study undertaken within the ambit this research group. This involved a baseline study[11] on the concentration of lead in ambient air in the vicinity of schools in a residential area, south of Durban. This was done by active sampling for 8 hour periods. The range of values for six sites was 0.03–0.83 $\mu g/m^3$. Compared to limits set by the European community[12] and the US EPA[13] of 2 $\mu g/m^3$ and 1.5 μ/m^3, respectively, these results were low. In view of the fact that this study was affected by factors such changing wind directions and rain, it was decided to investigate kerbside soils as a 'sink' for lead exhausted from motor vehicles. In spite of the fact that soluble lead may be carried away from the place where it was initially deposited, by rain or ground water, the results of the present study show that considerable amounts of lead are present in kerbside soils in urban, peri-urban and rural locations. The significance of these results is great in the light of the fact that many rural communities grow sustenance crops on roadside soils. A recent study[14] in France has shown that plants belonging to the *Graminaceae* family growing on roadside soil were found to have 2.1 mg/kg of lead.

Although the present study also had to contend with variables that are not easy to control, the data does enable one to make conclusions such as:

- the total lead found in acid- and microwave-digested kerbside soils is in the range of 163–923 ppm,
- only about half of the total lead is leached under acidic conditions,
- negligible amounts of lead are found at depths below 25 cm.

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