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THE CHEMICAL FORMS OF LEAD IN ROADSIDE DUSTS OF METROPOLITAN LAGOS, NIGERIA

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ABSTRACT

The chemical forms of lead in roadside dusts taken at several locations in the Lagos metropolis was investigated. Five fractions namely exchangeable, carbonate, Fe-Mn oxide, organic and residual were identified from the roadside dust samples by using a selective extractant speciation scheme. The Pb in each fraction was determined by flame atomic absorption spectrophotometric technique. The results obtained indicate that Pb in roadside dusts is primarily associated with the Fe/Mn hydrous oxide fraction. The results of the survey also indicated that less than 30% of the total Pb in the roadside dust was readily bioavailable.

Keywords: roadside dust, sequential extraction, lead, speciation, bioavailability.

INTRODUCTION

Of the three materials, soil, sediment and dust, which derive primarily from the Earth's crust, and with which human beings come into contact, dust is the most pervasive. Therefore, dust is an important pathway in human exposure to lead (Fergusson and Kim, 1991). Vehicular dust entrailment rate in Nigeria has been estimated to be 6.5g/vehicle-km for paved roads and 62g/vehicle-km for unpaved roads compared to only 0.1g/vehicle – km for streets in London, England (Akeredolu, 1989). However, dust has largely been ignored as a significant source of heavy metals in the African urban environment unlike in the developed countries where there is a growing awareness of the substantive contribution that dust can make to the levels of trace metals in humans (Evans et al., 1992; Fergusson and Kim, 1991). Young children have been identified as the highest risk group for two reasons. Firstly, young children are more likely to ingest significant quantities of dust than adults, and secondly, young children are usually more susceptible to a given intake of toxin than adults (Evans et al., 1992; Fergusson and Kim, 1991). "Pica" and repetitive hand or finger sucking are thought to be the two main dust ingestion routes (more or less) unique to children.

Lead pollution of the environment has become recognized as a public health hazard (Nriagu 1992; Nriagu et al., 1997a). The major source of lead in roadside soil and dusts has been attributed to the use of leaded petrol-driven vehicles. Lead contents of gasoline sold in African countries are now among the highest in the world; with typical concentrations found in the range of 0.5 - >1.0 g/l (Nriagu et al., 1997b). The average lead content of regular gasoline in Nigeria is about 0.74 g/l (Ogunsola et al., 1994). The major highways in Lagos carry tens of thousands of vehicles per day but during the rush hour traffic, the travelling speeds typically decrease to less than 10 km/hr for most roads (Akeredolu, 1989) which are clogged with motor bikes, cars and trucks. The poorly maintained vehicles emit blue plumes of bad odour and unburnt hydrocarbons (Baumbach et al., 1995) resulting in a large fraction of the lead in gasoline being released to the atmosphere (USEPA, 1986).

It has been recognized for many years that in many applications, a knowledge of the total level of metals present in a sample, although useful, is inadequate (Hill, 1992). This is because the toxicity, mobility and bioavailability of trace metals in soils and dusts are influenced by the physico-chemical form of the metal. For instance, Cr (111) is an essential trace element but Cr (VI) is toxic. In other words, the toxic effect of a metal is determined more by the type of chemical species present than its concentration. Therefore, in many applications, a knowledge of the chemical form of a trace element is becoming increasingly important in addition to its total concentration (Evans et al., 1992; Ure, 1991; Xingfu and Shokohifard, 1989).

The purpose of this study was to investigate the chemical forms of lead in roadside dusts of metropolitan Lagos. The degree of environmental hazard posed by dust to adults and children residing, schooling or working in and around busy Lagos major highways and byeways was also studied. The city of Lagos was the 22nd largest city in the World with a population of 5.5 million in 1991 (The Guardian, 1998). By 2025, Lagos will probably become the third largest city in the World with a population of 25 million people (The Guardian, 1998). With its 300 industries or 12 industrial estates, Lagos has over 60% of al industrial activities in Nigeria, and stands th

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greatest risk of being irreparably degraded by uncontrolled particulate emissions with concomitant deleterious health effects to man and living resources.

EXPERIMENTAL

Sampling and sampling site.

Roadside dust samples were collected from ten different areas of Lagos metropolis. On a typical working day, traffic will build up on this roads causing at times long tail backs. In addition, the sites are regular bus-stops for the municipal buses that convey tens of thousands of Lagosians to work. The samples were collected during the dry season (December, 1997) by carefully sweeping the dust along the roadsides and subsequently packing it into polythene bags. Each dust sample collected was carefully labelled immediately.

Sample Treatment.

Dust samples were first air dried (for about 24 hours) after which they were passed (separately) through a 850μm sieve. This was done to remove all large particles and dirt. Following this treatment, the dust samples were ground in a mortar and subsequently passed through a 250 μm sieve. The samples were then dried in the oven at 37°C for 7 days.

Sequential Extraction Method.

The sequential extraction procedure used was as developed by Tessier et al., (1979) which involves the separation of the extract from the residue by filtration followed by a thorough washing of the residue and drying at room temperature. Approximately 5g of the dried sample was accurately weighed out and treated as follows:

Step 1: Exchangeable Fraction

40ml 1M magnessium chloride solution was added to each sample. The mixture was continously agitated, with the aid of a mechanical shaker for 1 hr. The mixture was then filtered using a 45 μm filter paper. The filterate was retained for analysis and the residue washed with 40ml distilled water.

Step 2: Carbonate Bound Fraction

40ml 1M acetic acid/sodium acetate buffer of pH 5.0 was added to the residue obtained in step 1. The resulting mixture was then shaken continously (using mechanical shaker) for 5 hours. Afterwards, the mixture was filtered and the filterate retained for analysis. The residue was washed as in step 1

Step 3: Iron and Manganese Hydrous Oxides Fraction

100 ml 0.04M hydroxylamine hydrochloride in 25% acetic acid was added to the residue obtained in step 2. This solution was left in a water bath at 95°C for 6 hours stirring occasionally. After this time, the solution was filtered, retaining the filterate for analysis and the residue washed accordingly.

Step 4: Organic Bound Fraction

To the residue of step 3 was added 30ml 0.02M HNO_3 and 30% H_2O_2 at pH 2. The mixture was left in the water bath at 85°C for 5 hours, and occasionally agitated. After 2 hours, a second 20ml aliquot of the acidified H_2O_2 was added. After this treatment, 50ml 3.2M ammonium acetate in 20% nitric acid was added to the solution which was then diluted to 200ml with distilled water, mechanically shaken for 30 min and then filtered. The filterate was retained for analysis.

Step 5: Residual Fraction

The residual fraction was not determined due to non-availability of the required chemicals. Instead, the samples were digested for total lead as described below. After analysis, the residual fraction was taken as the difference between the total and the sum of the first four fractions.

Digestion Procedure for Analysis of Total Lead

2g of each dust sample was weighed carefully into a conical flask. To this was added 1ml perchloric acid followed by 50ml conc. nitric acid. The mixture was gently heated on a heating mantle and stirred occasionally. The mixture was heated to dryness and then allowed to cool, after which 50ml distilled water was added. This was then boiled for 30 seconds and subsequently filtered. The filterate was transferred into 100ml standard flask and then made up to mark with distilled water

Analysis

The supernatant was analysed for lead using a Buck Model 200A flame atomic absorption spectrophotometer. Blanks were run to assure quality control. Due care was taken to protect the samples from laboratory dust contamination. To ensure the validity of the data, some actions were taken to meet QA/AC requirements. The QA/QC program in this study included:

(a) Running triplicate samples

(b) Testing the analytical reproducibility at

Table 1: Mean values for chemical associations of lead in dusts (n=3). Lead levels are in µg g^{-1} of dry sample

Sample site		Exchangeable	Carbonate	Fe/Mn	Organic	Residual	Total
Mile 12	Mean	4.4	15.3	104.0	1.0	29.9	154.6
	S.D	0.6	0.1	2.8	0.3	0.9	4.3
	%	2.8	9.9	67.3	0.7	19.3	100.0
Yaba Central	Mean	4.0	32.5	108.0	8.0	39.3	191.8
	S.D	0.1	0.6	5.7	5.7	10.5	1.4
	%	2.1	16.9	56.3	4.2	20.5	100.0
Idumota	Mean	3.3	31.3	75.0	22.0	26.0	157.6
	S.D	0.1	0.1	1.4	42.8	2.8	1.4
	%	2.1	19.9	47.6	13.9	16.5	100.0
Mile 2	Mean	2.5	43.5	109.0	30.0	22.0	207.0
	S.D	0.1	0.1	4.2	8.5	11.5	7.1
	%	1.2	21.0	52.7	14.5	10.6	100.0
Oshodi	Mean	3.5	51.9	88.6	12.2	61.0	217.2
	S.D	0.1	1.0	2.1	0.3	4.4	7.1
	%	1.6	23.9	40.8	5.6	28.1	100.0
Ojota	Mean	3.7	19.2	68.0	0.8	13.3	105.0
	S.D	0.3	3.4	2.8	0.6	0.6	7.1
	%	3.5	18.3	64.8	0.8	12.6	100.0
Ojuelegba	Mean	3.5	15.6	101.0	13.6	6.3	140.0
	S.D	0.3	0.6	26.9	0.6	1.1	28.3
	%	2.5	11.1	72.2	9.7	4.5	100.0
Oyingbo	Mean	4.2	6.3	120.0	1.6	12.9	145.0
	S.D	0.7	0.1	14.1	0.6	8.4	7.1
	%	2.9	4.3	82.8	1.1	8.9	100.0
Tinubu Square	Mean	4.4	15.3	106.0	16.0	10.8	152.5
	S.D	0.6	0.1	14.1	5.7	4.3	3.5
	%	2.9	10.0	69.5	10.5	7.1	100.0
Tafawa Balewa Square	Mean	3.4	10.6	82.0	14.0	12.5	122.5
	S.D	0.2	0.1	5.7	2.8	5.3	3.5
	%	2.8	8.7	66.9	11.4	10.2	100.0

intervals by replicate analyses of a standard Pb solution. The coefficient of variation was 2.50% (n = 10)

(c) Checking the recoveries of standard solution spikes. The range of percentage recovery obtained in the study fell between 98 and 103%.

RESULTS AND DISCUSSION

Total Lead Levels.

The mean concentrations of lead in dusts for the roads sampled is given in Table 1. The results ranged from 105.0 to 217.2 µg Pb g^{-1} with a mean of 159 ± 36 µg Pb g^{-1}: Ajayi and Kamson (1983), previously reported that lead contents of Lagos roadside dusts can exceed 700 µg g^{-1}. The lower total lead levels obtained in this study may be due partly to the street cleaning regime that has been in operation for the past few years (introduced after 1983). In addition, the annual flooding episodes has worsened in the past few years. This can be attributed to the ever-increasing human population which has over-stretched the inadequate facilities provided for refuse and storm drainage. Consequently, the build-up of lead in roadside dust is prevented because the dust is regularly washed away. In addition, industrial activities have slowed down in the past few years. Most manufacturing industries are not producing at full capacity because of the poor economy. Infact a number of industries have folded up as a result of the down-turn in the economy. There is no doubt that this will have its own effect on the environment (even if it is minimal) particularly when compared to the oil-boom era of the seventies!. However, the results obtained in this study is in good agreement with the range of 50-300 μg g^{-1} reported by Nriagu (1992) as the typical concentration of lead in urban soils and dusts of African cities.

Comparing the results of each sampling site, Oshodi had the highest lead level. This was as expected because Oshodi is not only a big terminal bus-stop, but also a railway station and has a very big market that attracts thousands of people daily. Besides, Oshodi is surrounded by different industries which no doubt pollute the already dusty and dirty environment with lead and other heavy metals. On the other hand, Ojota had the lowest lead concentration when compared with the result of other sampling sites. However, the value of 105.0 μg Pb g^{-1} for Ojota is still relatively high. This may be as a result of the presence of two petrol-filling stations adjacent to the sampling site.

Sequential extraction.

The results obtained from the sequential extraction study (Fig. 1) indicate that most of the lead are tied up with the Fe/Mn hydrous oxide phase as shown below:

Phase	% Pb
Exchangeable	1.2 – 3.5
Carbonate	4.3 – 23.9
Fe/Mn hydrous oxide	40.8 – 82.8
Organic	0.7 – 14.5
Residual	4.5 – 28.1

The carbonate fraction was moderately significant in Oshodi and Mile 2 samples. The fraction can readily be related to the inorganic carbon content of the roadside dust samples and is strongly dependent on soil pH (Xingfu and Shokohifard, 1989). It was observed that both Oshodi and Yaba Central samples contained a substantial (>20%) amount of residual fraction. Generally, the data obtained indicated that the chemical forms of lead decreased in the following order of abundance:

Fe-Mn hydrous oxide > Residual > Carbonate > Organic > Exchangeable

The association of lead with the iron/manganese hydrous oxide fraction implies that this fraction remains an important repository of lead in dust samples such as in metropolitan Lagos which gives a serious cause for concern particularly with the continuous use of leaded petrol. Presently, the atmospheric lead emissions in Nigeria in recent years have been estimated to be 2800 metric tons per year with 90% of these derived from automobile tail pipe (Nriagu et al., 1997b; Obioh et al., 1988). The remaining 10% comes from industrial sources; the burning of fossil fuels, refuse and forests; careless and unauthorized disposal of unwanted materials (e.g. car battery, paint containers, etc); lead containing insecticides (e.g. lead arsenate) as well as civil engineering activities. The continuous addition of lead to petrol and the association of lead with iron/manganese hydrous oxide fraction of dusts may create long term contamination problems. This is because lead associated with this fraction can act as a reservoir for replenishing the store of more easily mobilized lead as this latter fraction becomes depleted (Gibson and Farmer, 1986).

The results obtained in this study is in agreement with the Glasgow and Lancaster partitioning data in identifying the environmentally important fractions for lead as iron and manganese oxide (Gibson and Farmer, 1986; Harrison et al., 1981). Fergusson and Kim (1991) confirmed from several studies that most of the lead (65 – 85%) are tied up with carbonate and amorphous iron/manganese hydrous oxide phases. Evans et al., (1992) also obtained similar results for the speciation pattern of lead in street dusts and soils sampled in the vicinity of two London schools.

Hazard assessment.

From previous reports (Chaney et al., 1988, Evans et al., 1992; Tessier et al., 1979; Xingfu and Shokohifard, 1989), it seems likely that dust samples which contain high amounts of lead in the exchangeable and carbonate fractions pose a greater risk than those samples with lesser amounts. This is because the two fractions (exchangeable and carbonate) are active forms which are easily mobilised and readily bioavailable while the other fractions are less active and less bioavailable. Chaney et al., (1988) reported that those materials which are readily soluble in weak acid solutions were found in acute rat feeding tests to be highly bio-available. The carbonate and exchangeable fractions are released into solutions of low pH of about 3.5 (Evans et al., 1992) which can be related to stomach conditions.

Table 2 gives some indication of the proportions of total lead that are possibly available in the acid solutions of the stomach. From the results, the proportion of the total Pb in the dust samples that could readily be mobilized easily is generally below 30%. In other words, a small percentage of the total Pb is potentially bio-available (i.e. in the exchangeable and carbonate forms) and over 75% of the total Pb in the dust is stable and immobilized.

Table 2: Prediction of % lead in the sampled roadside dusts of metropolitan Lagos that may be vio-available in the acid conditions of the stomach.

	Exchangeable +	Carbonate$^+$	Overall Total$^+$	% Available$^+$
Mile 12	4.4	15.3	154.6	12.7
Yaba Central	4.0	32.5	191.8	19.0
Idumota	3.3	31.3	157.6	22.0
Mile 2	2.5	43.5	207.0	22.2
Oshodi	3.5	51.9	217.2	25.5
Ojota	3.7	19.2	105.0	21.8
Ojuelegba	3.5	15.6	140.0	13.6
Oyingbo	4.2	6.3	145.0	7.2
Tinubu Square	4.4	15.3	152.5	12.9
Tafawa Balewa Square	3.4	10.6	122.5	11.4

+ In μg g^{-1} dry sample

$$\text{*\% Available} = \frac{\text{Exchangeable} + \text{Carbonate}}{\text{Total}} \times 100$$

CONCLUSION

The fraction of lead in the environment is an important factor in the assessment of the potential hazards associated with the metal by providing information on the bio and geo-availability of the metal and therefore the potential risk to living things. Obviously, the five-step sequential chemical extraction procedure provides considerable information on the extent and relative rates of release of Pb from dust under progressively more vigorous conditions of chemical attack. From the results obtained, it would appear that lead in roadside dusts of metropolitan Lagos is primarily associated with the iron/manganese hydrous oxide fraction.

The future persistence of lead in roadside dust can be predicted in view of the element's strong association with the less accessible, moderately reducible phase primarily through adsorption and binding to amorphous iron oxides and hydroxides. Therefore, while forthcoming legislation to reduce lead level in petrol or to eliminate anti-knock lead compounds altogether, will undoubtedly cause a substantial and rapid drop in atmospheric lead concentrations, surface soils/dust will remain highly contaminated with lead. This could have severe long-term environmental implications, including the maintenance of elevated levels of "available" lead via slow release from the moderately reducible phase and continuing contributions to the content of street dust, a notable source of lead exposure for young urban children.

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