

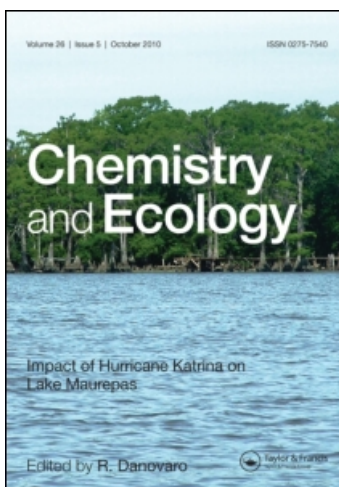
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## Speciation study of lead and manganese in roadside dusts from major roads in Ile-Ife, South Western Nigeria

A.O. Ogunfowokan<sup>a\*</sup>, J.A.O. Oyekunle<sup>a</sup>, L.M. Durosinmi<sup>a</sup>, A.I. Akinjokun<sup>b</sup> and O.D. Gabriel<sup>a</sup>

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A speciation study of Pb and Mn in roadside dust along major roads in Ile-Ife, South Western Nigeria, was investigated. Pb and Mn values obtained by total digestion ranged from  $22.23 \pm 3.52$  to  $43.48 \pm 3.05$   $\mu\text{g/g}$  and  $35.93 \pm 0.15$  to  $83.76 \pm 0.06$   $\mu\text{g/g}$ , respectively. The results of speciation analysis of Pb and Mn in the samples showed that the mean levels of these metals in the various fractions followed the order: organic matter > residual > Fe-Mn > carbonate > exchangeable and organic matter-bound > exchangeable > carbonate-bound > residual > Fe-Mn oxide-bound respectively. The speciation study therefore revealed that most of the Pb and Mn were associated with the organic matter fraction and that they were least available in the exchangeable and Fe-Mn oxide fractions, respectively. The apparent mobility and potential bioavailability for these metals in the road dust was Mn > Pb. There is a significant difference between the means of Pb and Mn in the road dust of the study area at  $p \leq 0.05$ , which strongly suggests that they may not have come from the same source; different sources may be responsible, which may be anthropogenic, such as tyre wear, vehicular emission, brake linings and natural.

**Keywords:** speciation analysis; road dust; lead; manganese; mobility factor

### 1. Introduction

Simple approaches for screening risk assessment use measurements of total contaminant concentrations. Such 'crude chemistry' has the potential of grossly overestimating the risk [1,2]. For full risk assessment, there is the need to know not just how much contamination is present, but it is essential to ascertain the chemical forms of the contaminant, including the amount of it that is bioavailable. Only then can stakeholders in environmental issues avoid taking deceitful and costly decisions. In recent times, the scientific community has concluded that toxicity, bioavailability, bioactivity, transport in organisms, biogeological distribution/transportation, and hence, the eventual impact of the toxic element in our environment will be dictated by the species of elements in a sample [3].

Both Pb and Mn are ubiquitous environmental heavy metals. Lead poisoning is usually ranked as the most common environmental hazard and its toxicity is widely documented. Health hazards

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of Pb include impairment of hearing ability, interference with the red blood cell formation, renal failure, and increased frequency of miscarriages and still births [4,5]. Other health hazards include a reduction in the body's immune system, low birth weight, premature birth, and reduced sperm count and motility [6–9]. On the other hand, Mn is an essential element. It is a constituent of certain enzymes and can also activate many enzymes. It has been shown to stimulate the synthesis of chondroitin sulphate, an important constituent of cartilage and connective tissues [10]. Maternal Mn deficiency has been demonstrated to cause skeletal abnormalities and impaired growth [11], ataxia and defective otoliths [12], dermatitis, pigment changes of hair, retarded hair growth and hypocholesteremia [13]. Furthermore, in humans, excessive exposure to Mn and its compounds has led to a variety of symptoms, some of which are irreversible [14]. Serious health hazards resulting from Mn toxicity include severe pathological disorders of the central nervous system that may manifest as a permanent crippling neurological disorder of the extra pyramidal system, similar to Parkinson's disease. Others are reproductive and immune system dysfunctions, nephritis, testicular damage, pancreatitis, lung disease and hepatic damage. In its milder form, the toxicity of Mn is expressed by aggressiveness, hallucinations, disturbances of the libido and improper coordination. Once established, these symptoms tend to persist even after the Mn body burden returns to normal [14].

Motor vehicles introduce a number of toxic metals into the atmosphere, which are later deposited on roadsides [15]. As a result of vehicle emissions, the deposition of manganese and other metals on the road may result in their incorporation into street dust due to their size, that ranges between  $10^{-9}$ – $10^{-6}$  m [16]. Street dusts have been shown to contain elevated levels of toxic metals that may emanate because of airborne redistribution by vehicles [17–20]. Of all the types of dust found in the urban environment, one of the most highly infiltrated with toxic metals is roadside dust. Since such dusts may be inhaled while airborne or discharged into rivers by storm-water washoff, roadside dust may hence represent a major pollution source within the urban environment [21].

The various ways in which heavy metals associate with soil components determines their mobility and bioavailability [22,23]. Thus, to provide reliable information on the forms of association of heavy metals regarding their availability levels and hence potential mobility to food and water sources, a sequential extraction procedure has been largely relied upon to partition heavy metals, such that their chemical reactivity can be elucidated [24].

On the basis of the information above, the chemical speciation of Pb and Mn from the total metal content in the roadside dust of Ile-Ife was established, as it may serve as a threat to plants, humans, and the whole environment. Our earlier study of Ile-Ife reported levels of lead, zinc and copper in *Barbula lambarenensis* from roadsides as a monitor of local atmospheric pollution of this ancient city in relation to the traffic density [15]. Although the results from the study showed higher levels of Pb and Zn in areas with relatively higher traffic density than low traffic density areas, no consideration was given to the forms in which these metals exist. Thus, the present study is an attempt to improve on the earlier one by studying the chemical speciation of Pb and Mn in the roadside dust of Ile-Ife as a monitor of atmospheric pollution and to ascertain whether there has been any reduction in the levels of vehicular Pb since the ban of leaded fuel in Nigeria. In order to realise the above-mentioned task, the sequential extraction method of Tessier et al. [25] was adopted in this paper, taking into account five fractions describing the type of metal combinations in the roadside dust. Street dust investigation is of particular importance because it is freely being inhaled by those traversing the streets and those residing within the vicinity of the streets; the more the dust on such streets becomes contaminated with heavy metals, the more people are exposed to the health hazards associated with such metals. On the other hand, the dust usually gets discharged in the adjoining rivers and marine environment during rainfall through surface runoff and could seriously pollute the water and concentrate in the surface sediments. This might prove toxic to aquatic life, and at worst it may contaminate fish or shellfish, which could have directly adverse

impact on the health of individuals who consume seafood. Aged cars, trucks and mini-buses are responsible for most of the air pollution in this ancient city; there are no industries in the study area.

## 2. Materials and methods

### 2.1. Sample collection and pre-treatment

Ten sampling sites along major roads in Ile-Ife with heavy traffic density were selected for this study. The sites were Sabo, Fajuyi, Phase I of Obafemi Awolowo University (OAU) Teaching Hospital Complex, Opa, Olonade, Diganga Hotel, Ibadan Road Toll Gate, the School of Science (Ondo Road), Our Lady High School Junction and the Sports Centre (OAU). The geographical locations of these sites were determined using GPS-Magellan GPS 3010. A map of the study area is presented in Figure 1, showing South Western Nigeria, the road network of Ile-Ife, Osun state in Nigeria and the sampling sites. Sampling took place monthly from October 2006 to March 2007. The geological settings and minerals of the study area consist of schists, granite, an abundance of gniesses, and amphibolites.

Approximately 10 g of street dust was collected from five spots at 10 m apart within a given site by gently sweeping the road approximately 3 m from the edge with a clean plastic dustpan and brush. Dust samples from each site were made into composite representative samples and stored in sealable propylene bags. Dust was not collected adjacent to site-specific pollution sources such as gasoline sites, and there are no industries in the town under investigation. The samples were air-dried over an inert surface in a ventilated cupboard to minimise cross contamination of samples. The dried samples were sieved through a polythene mesh of 2 mm pore size to get rid of

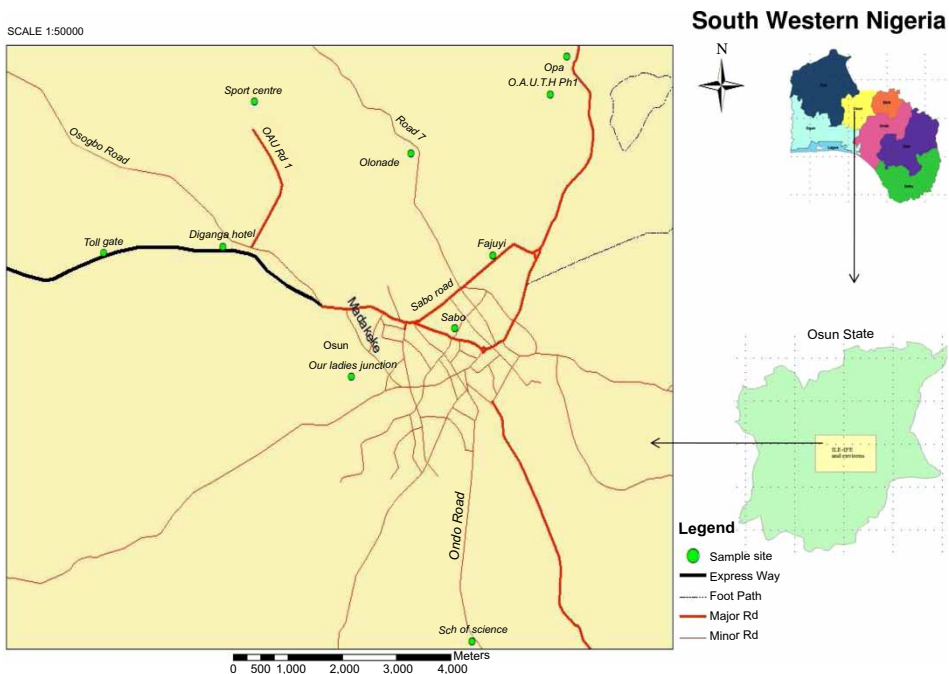


Figure 1. The location of the sampling sites.

pebbles and large particles. Further air-drying was completed before samples were selected by a coning and quartering method.

## 2.2. Apparatus and reagents used

All glass, polypropylene tubes and Teflon beakers used were first washed with liquid detergent, rinsed with tap water and distilled water, and then soaked in 10% HNO<sub>3</sub> (v/v) for 48 h. They were then re-washed with liquid detergent and rinsed thoroughly with doubly distilled water. Thereafter, the apparatus were oven-dried for 12 h at a temperature of 80°C. All the reagents used, viz. HNO<sub>3</sub> (Riedel-deHaën, Germany), HCl (Sigma-Aldrich, Germany) and HF (British Drug House (BDH) Chemicals Ltd, Poole, England), were of analytical grade.

## 2.3. Determination of total lead and manganese

A 2.5 g dust sample was digested in Teflon beakers with 30 mL aqua regia (HCl:HNO<sub>3</sub>; 3:1) on a thermostatted hot-plate between 150 and 180°C. The content of the Teflon beaker was replenished as necessary with more aqua regia to avoid total evaporation. After about 2 h of digestion, the Teflon beaker with its content was brought down from the hot-plate to simmer. Then, 5 mL HF was added and digested for a further 30 min. The Teflon beaker with the content was allowed to cool down to room temperature before the content was quantitatively transferred into a 25 mL volumetric flask and made up to the mark with doubly distilled water. A blank determination was carried out using the procedure described above without the sample.

The Pb and Mn contents were determined using Atomic Absorption Spectrophotometer (AAS) (ALPHA 4 Chemtech Analytical UK) at the Centre for Energy Research and Development (CERD), Obafemi Awolowo University, Ile-Ife, Nigeria.

## 2.4. Sequential extraction of lead and manganese from road dusts

The sequential extraction procedure of Tessier et al. [25] was used for the extraction and partitioning of Pb and Mn into exchangeable, bound to carbonate, bound to Fe-Mn oxides, bound to organic matter and residual fractions in this study. Then 2.5 g of airdried and homogenised dust sample of  $\leq 2.0$  mm diameter particle size was subjected to various leaching treatments to separate the heavy metals into the five operationally defined fractions. All extractions were performed in 50 mL polypropylene centrifuge tubes. The resulting supernatant aqueous layer was carefully filtered into analytical vials and taken for AAS determination of Pb and Mn.

### 2.4.1. Exchangeable (F1)

The weighed sample was extracted at room temperature with 20 mL 1M MgCl<sub>2</sub> (pH 7) with continuous agitation for 1 h.

### 2.4.2. Carbonate-bound (F2)

The residue from F1 was treated at room temperature with 20 mL 1M NaOAc adjusted to pH 5 with HOAc. Continuous agitation was maintained for 5 h.

#### 2.4.3. *Fe-Mn oxides-bound (F3)*

The residue from F2 was extracted with 40 mL 0.04M NH<sub>2</sub>OH.HCl in 25% (v/v) HOAc at 96 ± 1°C with occasional agitation for 5 h.

#### 2.4.4. *Bound to organic matter (F4)*

To the residue from F3 was added 7.5 mL of 0.02M HNO<sub>3</sub> and 12.5 mL of 30% H<sub>2</sub>O<sub>2</sub> adjusted to pH 2 with HNO<sub>3</sub>. The mixture was heated to 85°C for 2 h with occasional agitation. A second 7.5 mL aliquot of 30% H<sub>2</sub>O<sub>2</sub> was added and heated further for 3 h at 85°C with intermittent agitation. After cooling, 12.5 mL of 3.2M NH<sub>4</sub>OAc in 20% (v/v) HNO<sub>3</sub> was added to prevent the adsorption of extracted metals into the oxidised sediments and the mixture was diluted to 40 mL. Continuous agitation for 30 min followed.

#### 2.4.5. *Residual (F5)*

The residue from F4 was digested with 15 mL concentrated HNO<sub>3</sub> and later refluxed for 1 h, filtered and washed with 10 mL of hot 3M HNO<sub>3</sub>.

### 2.5. *Mobility factor (MF) determination*

The MF, an index of potential mobility of metal ions in soil [26,27], was determined on the basis of the absolute and relative values of fractions (F1 and F2) weakly bound to soil components using the relationship:

$$MF = \frac{F1 + F2}{F1 + F2 + \dots + F5} \times 100.$$

### 2.6. *Quality assurance protocol*

#### 2.6.1. *Blank determination*

Alongside each determination was a blank prepared to check for background levels of Pb and Mn in the reagents used for various leaching procedures.

#### 2.6.2. *Recovery analysis*

This was conducted to ascertain the precision of the analytical procedures used in this study, since reference soil material was not available to us when this study was carried out. A 1 g road dust sample was put into a Teflon beaker in the presence of 6 mL HNO<sub>3</sub> acid. This was spiked with 50 mL of 50 µg/mL of Pb<sup>2+</sup> and Mn<sup>2+</sup> and digested using the method already described. The digested spiked sample was made up to the mark in a 50 mL volumetric flask with doubly distilled water. Also, a 50 mL each of 50 µg/mL of the standard Pb<sup>2+</sup>, Mn<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> solutions were taken for AAS analysis. The results obtained were compared with those of the spiked soil samples to obtain the recovery of the analysis. Triplicate analysis was carried out to further check the reproducibility of the methods used in this study.

Generally, the quality control performed included daily analyses of standards and triplicate analyses of samples and blanks. The instrument was calibrated using the method of standard addition in order to reduce matrix effect.

## 2.7. Data analysis

The standard deviation for manganese and lead from three replicate measurements was determined. General subsequent evaluation of the data was done using the mean values. Student's *t*-test was used to demonstrate the significant difference between two means of Pb and Mn.

## 3. Results and discussion

Table 1 gives the geographical locations of the sampling sites. The study area lies within longitudes 4°29'50" to 4°34'29" E and latitudes 7°26'30" to 7°31'21" N, while the land elevation is within 242.5 ± 10.8 and 286.2 ± 9.2 m above sea level. The average traffic density was between 355 and 962 vehicles per h. Table 2 contains the results of the recovery analyses conducted. From the results, the analytical procedures were adjudged reliable, with the recovery analysis showing percentage recoveries of 85.38 ± 7.31% for Pb and 94.70 ± 6.21% for Mn.

The total metal levels of Pb and Mn contained in the samples from each site reflect varied degrees of contamination, as presented in Table 3. The values of Pb ranged from 22 ± 3.52 to 43.48 ± 3.05 µg/g, yielding an overall mean of 35.54 ± 5.91 µg/g, while levels of Mn ranged from 35.93 ± 0.15 to 83.76 ± 0.06 µg/g, yielding an overall mean of 51.46 ± 15.10 µg/g. In general, the highest levels of Pb (43.48 ± 3.05 µg/g) correspond to samples from Sabo road dust, with an average traffic volume of 771 vehicles h<sup>-1</sup>, while for Mn the highest value (83.76 ± 0.06 µg/g) corresponds to samples from Opa road dust, with an average traffic volume of 562 vehicles h<sup>-1</sup> (Tables 1 and 3). Although the levels of Pb in the study area were generally low but higher in areas with relatively high traffic volume, the levels obtained in this study (22.23 ± 3.52 to 43.48 ± 3.05) µg/g were lower than those reported in our earlier study of 2004 (196.8 ± 0.04 to 108 ± 0.03) µg/g [15] monitoring local atmospheric pollution of this ancient city in relation to traffic density.

Table 1. Geographical locations of the sampling sites.

| Sampling Site       | GPS Grid Coordinate |               | Elevation (m) | Average traffic volume* |
|---------------------|---------------------|---------------|---------------|-------------------------|
|                     | Latitude (N)        | Longitude (E) |               |                         |
| Olonade             | 7°30'33"            | 4°32'55"      | 273.4 ± 9.2   | 355                     |
| Sabo                | 7°29'6"             | 4°33'21"      | 262.0 ± 13.4  | 771                     |
| Fajuyi              | 7°29'42"            | 4°33'44"      | 281.7 ± 11.4  | 713                     |
| OAUTHC Phase I      | 7°31'2"             | 4°34'19"      | 258.1 ± 8.7   | 962                     |
| Opa                 | 7°31'21"            | 4°34'29"      | 268.7 ± 11.0  | 562                     |
| Sport Centre        | 7°30'59"            | 4°31'21"      | 276.7 ± 9.6   | 773                     |
| Diganga Hotel       | 7°29'47"            | 4°31'2"       | 254.8 ± 13.9  | 788                     |
| Toll Gate           | 7°29'44"            | 4°29'50"      | 242.5 ± 10.8  | 534                     |
| Our Ladies Junction | 7°28'42"            | 4°32'19"      | 257.8 ± 9.0   | 622                     |
| School of Science   | 7°26'30"            | 4°33'31"      | 286.2 ± 9.2   | 470                     |

Note: \*Vehicles per hour.

Table 2. Results of recovery analysis.

| Metal species    | Amount spiked (µg/g) | Amount measured (µg/g) | % Recovery <sup>#</sup> |
|------------------|----------------------|------------------------|-------------------------|
| Pb <sup>2+</sup> | 50                   | 42.69 ± 3.12           | 85.38 ± 7.31            |
| Mn <sup>2+</sup> | 50                   | 47.35 ± 2.94           | 94.70 ± 6.21            |

Note: <sup>#</sup>Values are means of triplicate analysis ± standard error.

Table 3. Total lead and manganese levels in the road dust of Ile-Ife.

| Sampling Site     | Concentration ( $\mu\text{g/g}$ ) |                   |
|-------------------|-----------------------------------|-------------------|
|                   | Pb                                | Mn                |
| Olonade           | 22.23 $\pm$ 3.52                  | 48.94 $\pm$ 1.01  |
| Sabo              | 43.48 $\pm$ 3.05                  | 37.29 $\pm$ 0.14  |
| Fajuyi            | 34.53 $\pm$ 6.62                  | 58.58 $\pm$ 0.12  |
| Sport Centre      | 34.48 $\pm$ 3.96                  | 58.82 $\pm$ 0.14  |
| OAUTHC Phase I    | 33.38 $\pm$ 4.47                  | 63.62 $\pm$ 0.10  |
| Opa               | 35.34 $\pm$ 2.91                  | 83.76 $\pm$ 0.06  |
| Diganga Hotel     | 40.01 $\pm$ 2.00                  | 41.12 $\pm$ 0.07  |
| Toll Gate         | 41.44 $\pm$ 2.37                  | 37.55 $\pm$ 1.02  |
| Our Lady Junction | 37.78 $\pm$ 1.47                  | 48.98 $\pm$ 0.24  |
| School of Science | 32.73 $\pm$ 1.25                  | 35.93 $\pm$ 0.15  |
| Mean $\pm$ SD     | 35.54 $\pm$ 5.91                  | 51.46 $\pm$ 15.10 |
| $t_{\text{calc}}$ | 3.105                             |                   |

Notes:  $t_{\text{calc}}$  = calculated  $t$ -value;  $t_{\text{critical}}$  = 2.262 at 95% probability level. Values = mean of triplicate analysis  $\pm$  SD.

This data is evidence of the compliance of the petrochemical industry in Nigeria to produce unleaded fuel. However, the range of values of Pb reported for road dust in this study were much lower than the values (146–1620 mg/kg) reported for soils of contaminated battery and iron smelting industrial areas (Table 4) of Southern Nigeria [24], but within the range reported for the urban soils of Osogbo (9.8–136.1  $\mu\text{g g}^{-1}$ ) [32] and Port Harcourt (15.9–169.5  $\mu\text{g g}^{-1}$ ) [33], also in Nigeria. The mean levels of lead from this work were lower than those reported for street dust and roadside soils from other countries (Table 4), such as urban (386.9  $\mu\text{g g}^{-1}$ ), industrial dusts (273.9  $\mu\text{g g}^{-1}$ ) and peripheral sites (120.8  $\mu\text{g g}^{-1}$ ) of the Kavala region, Greece [30], Mission Peninsula, Michigan (soil) (90–210  $\mu\text{g g}^{-1}$ ) [34], Dhaka City, Bangladesh (53.3  $\mu\text{g g}^{-1}$ ) [35] and Spain (soil) (46–95  $\mu\text{g g}^{-1}$ ) [31], but match the range found in Elazig, Turkey (soil) (2.8  $\pm$  0.3–45  $\pm$  3.7  $\mu\text{g g}^{-1}$ ) [36]. The reasons for the higher levels of lead reported for other countries compared to Ile-Ife are likely to be due to of urbanisation, industrialisation and higher automobile exhaust levels due to higher traffic volume reported for the former. Ile-Ife is an ancient city with no industrialisation. However, it is important to note that automobile exhausts are likely to be the main contributive factor for the elevated lead levels, as all the samples were collected from major roads. Furthermore, the range of values of Mn reported for Spanish soil (366–1815  $\mu\text{g g}^{-1}$ ) [31] (Table 4) are much higher than those of our findings in this study. Tyre wear and brake linings may have contributed to the manganese concentrations obtained in the present study, since manganese and other metals have been reported to be present in these materials [28], especially as there is an absence of industrial activity in the study area. Results of a Student's  $t$ -test (Table 3) showed that there is a significant difference between the overall means of Pb and Mn in the road dust of the study area at a 95% probability level and  $n = 9$  degree of freedom ( $t_{\text{calculated}}$  (3.105) >  $t_{\text{critical}}$  (2.262)); this strongly suggests that the two analytes may not have come from the same source.

Table 4. Levels of lead and manganese ( $\mu\text{g g}^{-1}$ ) in street dust and roadside soil samples reported elsewhere.

| Area       | Pb   | Mn             |
|------------|--|----------------|
| Urban area | #386.9 $\pm$ 244.5; *(46–95); <sup>o</sup> (9.8–136.1); <sup>s</sup> {15.9–169.5}; <sup>+</sup> 90–210 | *(366–1815)    |
| Industrial | #273.9 $\pm$ 121.3; @146–1620; <sup>o</sup> (53.3)   | No information |
| Peripheral | #120.8 $\pm$ 55.3; <sup>o</sup> {2.8 $\pm$ 0.3–45 $\pm$ 3.7}   | No information |

Notes: #Kavala region, Greece [30]; @Southern Nigeria (soil) [24]; \*Spain (soil) [31]; <sup>o</sup>Osogbo (soil), Nigeria [32]; <sup>s</sup>Port Harcourt Metropolis, Nigeria (soil) [33]; <sup>+</sup>Mission Peninsula, Michigan (soil) [34]; <sup>o</sup>Dhaka City, Bangladesh [35]; <sup>o</sup>Elazig, Turkey (soil) [36].



Different sources may be responsible, which may be anthropogenic and natural. Although the total content of polluted elements in the soil can be useful for the characterisation of contamination intensity, the speciation of heavy metals with selective extracting agents gives further information about the fundamental reactions that govern the behaviour of metals in soils [24]. In this study, results of speciation analysis of Pb in the samples (Table 5) gave the overall mean amount of Pb in the following decreasing order: organic matter > residual > Fe-Mn > carbonate > exchangeable. That most of the Pb resided in the organic and residual fractions is probably due to the high retention capability of organic matters like humic acids and fulvic acids and the silicates in the residual fraction, since the tendency of such particulates to be adsorbed by the soil depends on the cation exchange capacity and organic composition of the soil [29]. More specifically, the values of Pb ranged from ND in the carbonate-bound fraction (F1) at Olonade, the Sports Centre and Our Lady High School Junction to  $15.78 \pm 1.44 \mu\text{g/g}$  in the organic-bound fraction (F4) at Sabo. The results in Table 5 therefore show that for the ten sites studied, the highest individual site mean of extractable lead in the street dust was associated with the organic matter fraction (F4) along Sabo Road.

The values of mobility factor (MF) for Pb (Table 7), with an overall mean of  $20.70 \pm 10.10$ , decreased in the following order: Fajuyi (40.58) > Toll Gate (31.93) > Diganga Hotel (28.10) > OAU Teaching Hospital Complex Phase I (21.72) > Olonade (19.35) > Opa (18.38) > Sports Centre (13.50) > Sabo (13.44) > School of Science (10.73) > Our Lady High School Junction (9.31). Apart from reflecting the levels of exchangeable and carbonate-bound Pb in this study, high MF values, an indication of lability and biological availability of heavy metals [26], showed the extent of the vulnerability of living things generally to heavy metals. Evidently, the inhabitants of the Fajuyi environment in this study have the highest vulnerability to Pb exposure, while those living around Our Lady High School Junction have the least vulnerability. The low MF value reported for lead in the road dust of Our Lady High School Junction is therefore an index of the high stability of this metal in the sample.

The result of speciation analysis of Mn in Table 6 further shows that the mean levels of Mn in the various fractions were: organic matter-bound > exchangeable > carbonate-bound > residual > Fe-Mn oxide-bound. The high level of Mn in the organic bound fraction may be attributed to the ease of complexation and peptisation products formed between the metal and natural organic matters like humic and fulvic acids. The low content of Mn in the residual and Fe-Mn oxide fractions was probably due to the low association or retention ability of the mineral's crystal structure, such as with detrital silicates and resistant sulphides. Generally, results of the speciation study reveal that the highest levels of both lead and manganese in the road dust of the study area

Table 5. Lead levels ( $\mu\text{g/g}$ ) in different chemical fractions of road dust in Ile-Ife.

| Sampling Site         | Exchangeable (F1) | Carbonate-bound (F2) | Fe-Mn oxide-bound (F3) | Organic matter-bound (F4) | Residual (F5)    | Total            |
|-----------------------|-------------------|----------------------|------------------------|---------------------------|------------------|------------------|
| Olonade               | ND                | $4.12 \pm 0.60$      | $3.07 \pm 0.85$        | $6.56 \pm 0.71$           | $7.54 \pm 1.17$  | $21.29 \pm 2.22$ |
| Sabo                  | $2.04 \pm 0.40$   | $3.39 \pm 0.62$      | $7.29 \pm 2.20$        | $15.78 \pm 1.44$          | $11.90 \pm 2.20$ | $40.40 \pm 4.69$ |
| Fajuyi                | $6.36 \pm 0.83$   | $8.28 \pm 2.02$      | $6.56 \pm 1.02$        | $10.45 \pm 0.91$          | $4.43 \pm 1.00$  | $36.08 \pm 3.11$ |
| Sport Centre          | ND                | $4.06 \pm 0.60$      | $5.98 \pm 1.22$        | $10.50 \pm 0.83$          | $9.54 \pm 1.68$  | $30.08 \pm 3.09$ |
| OAUTHC Phase I        | $1.06 \pm 0.10$   | $6.02 \pm 0.83$      | $8.06 \pm 0.93$        | $11.36 \pm 2.76$          | $6.10 \pm 0.88$  | $32.60 \pm 3.35$ |
| Opa                   | $1.20 \pm 0.10$   | $4.60 \pm 0.60$      | $10.62 \pm 1.21$       | $9.05 \pm 0.95$           | $6.08 \pm 2.18$  | $31.55 \pm 3.07$ |
| Diganga Hotel         | $1.84 \pm 0.11$   | $9.13 \pm 2.02$      | $4.99 \pm 0.04$        | $10.15 \pm 1.41$          | $12.93 \pm 4.01$ | $39.04 \pm 4.74$ |
| Toll Gate             | $2.06 \pm 0.40$   | $11.02 \pm 2.11$     | $6.33 \pm 0.21$        | $10.64 \pm 1.44$          | $10.91 \pm 4.19$ | $40.96 \pm 4.33$ |
| Our Lady Junction     | ND                | $3.17 \pm 0.60$      | $12.35 \pm 1.25$       | $10.15 \pm 1.04$          | $8.39 \pm 4.25$  | $34.06 \pm 4.34$ |
| School of Science     | $1.28 \pm 0.12$   | $2.14 \pm 0.40$      | $9.90 \pm 2.01$        | $10.60 \pm 0.96$          | $8.04 \pm 2.09$  | $31.86 \pm 3.27$ |
| Overall Mean $\pm$ SD | $1.58 \pm 1.87$   | $5.59 \pm 2.93$      | $7.52 \pm 2.79$        | $10.52 \pm 2.73$          | $8.59 \pm 2.74$  | 33.59            |

Note: Values = mean of triplicate analysis  $\pm$  SD.

Table 6. Manganese levels ( $\mu\text{g/g}$ ) in different chemical fractions of road dust in Ile-Ife.

| Sampling Site         | Exchangeable (F1) | Carbonate-bound (F2) | Fe-Mn oxide-bound (F3) | Organic matter-bound (F4) | Residual (F5)    | Total            |
|-----------------------|-------------------|----------------------|------------------------|---------------------------|------------------|------------------|
| Olonade               | 14.43 $\pm$ 0.01  | 8.70 $\pm$ 0.29      | 10.17 $\pm$ 1.05       | 3.05 $\pm$ 0.13           | 14.02 $\pm$ 0.05 | 50.37 $\pm$ 1.52 |
| Sabo                  | 6.27 $\pm$ 0.07   | 12.99 $\pm$ 0.06     | 5.23 $\pm$ 0.17        | 9.00 $\pm$ 0.10           | 3.76 $\pm$ 0.48  | 37.25 $\pm$ 0.88 |
| Fajuyi                | 12.81 $\pm$ 0.02  | 13.46 $\pm$ 0.00     | 4.65 $\pm$ 0.29        | 22.90 $\pm$ 0.02          | 4.64 $\pm$ 0.02  | 58.46 $\pm$ 0.35 |
| Sport Centre          | 14.95 $\pm$ 0.29  | 10.08 $\pm$ 0.09     | 3.28 $\pm$ 0.11        | 17.14 $\pm$ 0.12          | 12.04 $\pm$ 0.04 | 57.49 $\pm$ 0.65 |
| OAUTHC Phase I        | 14.62 $\pm$ 0.11  | 13.04 $\pm$ 0.04     | 8.33 $\pm$ 0.21        | 12.91 $\pm$ 0.52          | 10.42 $\pm$ 0.10 | 59.32 $\pm$ 0.98 |
| Opa                   | 24.62 $\pm$ 0.30  | 18.19 $\pm$ 0.07     | 10.02 $\pm$ 1.07       | 19.52 $\pm$ 0.29          | 8.92 $\pm$ 0.02  | 81.27 $\pm$ 1.75 |
| Diganga Hotel         | 12.24 $\pm$ 0.01  | 14.38 $\pm$ 0.04     | 3.12 $\pm$ 0.09        | 19.31 $\pm$ 0.02          | 2.23 $\pm$ 0.05  | 51.28 $\pm$ 0.21 |
| Toll Gate             | 12.04 $\pm$ 0.21  | 13.42 $\pm$ 0.01     | 2.03 $\pm$ 0.10        | 8.70 $\pm$ 0.01           | 2.11 $\pm$ 0.30  | 38.30 $\pm$ 0.63 |
| Our Lady Junction     | 19.10 $\pm$ 1.60  | 12.50 $\pm$ 0.10     | 3.56 $\pm$ 0.13        | 9.17 $\pm$ 0.36           | 2.50 $\pm$ 0.22  | 46.83 $\pm$ 1.41 |
| School of Science     | 6.38 $\pm$ 0.09   | 8.36 $\pm$ 0.11      | 0.97 $\pm$ 0.10        | 18.23 $\pm$ 0.15          | 1.28 $\pm$ 0.13  | 35.22 $\pm$ 0.58 |
| Overall Mean $\pm$ SD | 13.75 $\pm$ 6.94  | 12.51 $\pm$ 2.90     | 5.14 $\pm$ 3.28        | 13.99 $\pm$ 6.36          | 6.19 $\pm$ 4.71  | 51.58            |

Note: Values = mean of triplicate analysis  $\pm$  SD.

Table 7. Values of mobility factor (MF) of Pb and Mn.

| Site Name         | MF for Pb (%)     | MF for Mn (%)    |
|-------------------|-------------------|------------------|
| Olonade           | 19.35             | 45.92            |
| Sabo              | 13.44             | 51.70            |
| Fajuyi            | 40.58             | 44.94            |
| Sport Centre      | 13.50             | 43.54            |
| OAUTHC Phase I    | 21.72             | 46.63            |
| Opa               | 18.38             | 52.68            |
| Diganga Hotel     | 28.10             | 51.91            |
| Toll Gate         | 31.93             | 66.48            |
| Our Lady Junction | 9.31              | 67.48            |
| School of Science | 10.73             | 41.85            |
| Mean $\pm$ SD     | 20.70 $\pm$ 10.10 | 51.31 $\pm$ 9.04 |

occurred in the organic matter fraction. It is worth noting, however, that organic-bound fractions might contribute to environmentally available metals because of their lability when subjected to varying physicochemical weathering variabilities like elevated temperature, pH and redox potential (Eh) changes. Thus, considering the organic forms of these metals in addition to other forms like exchangeable and carbonate-bound obtained in this study, the percentage of Pb and Mn biologically available might be up to 52.35 and 78.03%, respectively.

The mobility factor (MF) for Mn in Table 7 in this study with an overall mean value of  $51.31 \pm 9.04$ , ranged from 41.85 at the School of Science to 67.48 at Our Lady High School Junction, were generally higher than those for Pb. Hence, Mn is more bioavailable than Pb. In terms of toxicity, however, levels of Pb may give cause for concern even at lower concentrations compared to Mn, and the effects may be several-fold higher than those of the Mn equivalents. Although manganese is primarily considered an essential element, excessive exposure to it, however, can lead to very serious health problems [14]. The overall mean levels of Pb ( $\mu\text{g/g}$ ) in the fractions were F1 ( $1.58 \pm 1.87$ ), F2 ( $5.59 \pm 2.93$ ), F3 ( $7.52 \pm 2.79$ ), F4 ( $10.52 \pm 2.73$ ) and F5 ( $8.59 \pm 2.74$ ), while the overall Mn mean levels ( $\mu\text{g/g}$ ) in the fractions were F1 ( $13.75 \pm 6.94$ ), F2 ( $12.51 \pm 2.90$ ), F3 ( $5.14 \pm 3.28$ ), F4 ( $13.99 \pm 6.35$ ) and F5 ( $6.19 \pm 4.71$ ) (Tables 5 and 6). The trend is illustrated by Figure 2. There are indications that the levels of Pb in the figure increased from F1 to F4 and decreased from there to F5, while that of Mn decreased from F1 to F3, increased from F3 to F4 and finally decreased from F4 to F5, showing two peak maxima for the two metals in the organic matter fraction (F4). Thus, it appears that the factors responsible for the binding of Pb and Mn among fractions in this study are antagonistic; while they enhance a stronger bond for

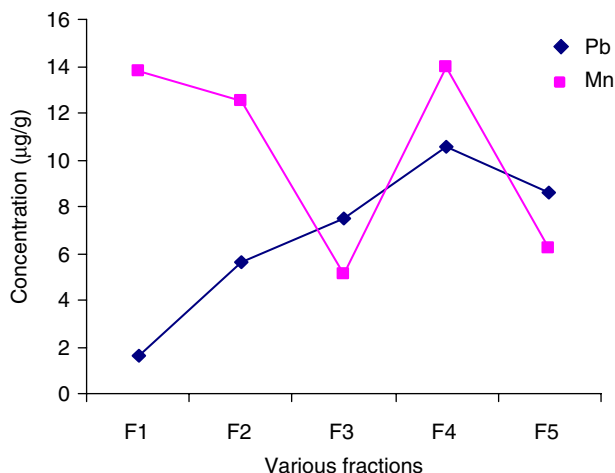


Figure 2. Variations in concentrations of Pb and Mn from different fractions.

one, they weaken it for the other. However, the binding behaviour seems similar between F3 and F5 for both analytes. Our results for exchangeable Pb differ from the previous findings of Olajire et al. [24], in which Pb levels were highest in the residual fraction. The low levels of lead reported in this study are indications of the compliance of the petrochemical industry in the country in the production of unleaded fuel.

#### 4. Conclusion

The levels and a speciation study of Pb and Mn of road dust in Ile-Ife have been investigated. The undertaken speciation study of Pb and Mn in the road dust revealed differences between these elements in the preferential formation of chemical combinations. There are indications that the Pb and Mn detected were mainly associated with the organic matter fraction in the road dust. The next most abundant fractions were exchangeable and carbonate bond for Mn and residual and Fe-Mn oxide bound for Pb.

The lowest available Pb and Mn were found in the exchangeable and Fe-Mn oxide fractions, respectively. The distribution of the studied metals in the various fractions and results of mobility factors confirm their differences in mobility and bioavailability. There are indications that sources of these metals are mainly anthropogenic, which may include tyre wear, brake lining and vehicular emissions, aside from natural sources. Further work on industrialised cities with higher traffic volume based on seasonal variations and comparison of results of the metal speciation with those of the study area is recommended for future investigations.

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