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Chemical Speciation and Distribution of Trace Metals in Roadside Soil from Major Roads in Iwo, a Semi-Urban City, South Western Nigeria

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ABSTRACT

A chemical speciation study of five trace metals (Fe, Mn, Zn, Pb and Cd) in roadside topsoil along nine major roads in Iwo, a semi-urban city, South-Western Nigeria, was investigated using Atomic Absorption Spectrophotometry. The mean values (µg/g) obtained by total digestion were in the following order: Fe (173.00 ± 11.64) > Mn (104.52 ± 10.01) > Zn (51.64 ± 2.60) > Pb (0.89 ± 0.06) > Cd (0.41 ± 0.03). The result of the speciation analysis showed that most of the Mn and Fe were associated with Mn-oxide bound followed by organic matter; Zn was associated with organic matter (OM) followed by exchangeable fractions while Pb and Cd showed a similar pattern for all the fractions. The physicochemical parameters studied showed that the soil was alkaline in nature. Pearson's correlation analysis showed that OM was positively correlated with $CaCO_3$ at $P < 0.01$; OM and $CaCO_3$ were negatively correlated with Mn at $P < 0.05$. A significant positive correlation was observed between the trace metals examined in this study. The mean values of the mobility factor (MF) for the five trace metals studied were Mn (41.70 ± 2.45), Pb (44.67 ± 1.57), Cd (43.88 ± 3.21), Fe (42.88 ± 1.54) and Zn (44.28 ± 1.54). The results of the calculated I-geo values for the street dusts of the study area showed that the roadside soil was practically unpolluted with Mn, Fe and Pb but moderately to heavily polluted with Cd. Even though the analytical results indicate that the levels of trace metals studied were below those indicated in the literature for typical soil, with the exception of Cd, future environmental monitoring is highly recommended.

Keywords: atomic absorption spectrophotometer, geo-accumulation index, mobility factor, pollution, vehicles

INTRODUCTION

The role of trace metals in the soil is increasingly becoming an issue of global concern at private and governmental levels, especially as soil constitutes a crucial component of rural and urban environment (USDA 2001) and can be considered as a very important "ecological crossroad" in the landscape (Thuy *et al.* 2000).

Urban roadside topsoil are the recipients of large amount of pollutant from variety of sources including industrial wastes, vehicle emissions, coal burning waste as well as other activities (Wang 2009). Besides this, among the sources of metals in road environment, traffic emissions from vehicles, lorries, and motor cycles have been identified to introduce a number toxic metals into the atomsphere which are later deposited on roadsides (Ogunfowokan *et al.* 2004, 2009; Okunola *et al.* 2011a). Ogunfowokan *et al.* (2009) reported that there was significant difference between the means of Pb and Mn in the road dust of the study area at $P < 0.05$, which strongly suggests that they may not have come from the same source. Different sources that may be responsible can include anthropogenic such as tyre wear, vehicular emission, brake linings and natural. Okunola *et al.* (2011a) reported a positive correlation between the metals (Cd and Pb) and traffic. The authors confirmed the fact that automobiles are major source of the presence of these metals in the roadside environment. Moreover, the result of their study showed that the concentrations in the mobile phase were generally high for Cd and Pb with the highest obtained during warm and wet and warm and dry seasons. The authors, therefore, suggested that these metals are potential toxic to residential and food vendors adjacent to the major roads in Kano metropolis. Nigeria is a developing country and the government is aiming at creating more roads as well as improving the quality of the existing roads, which in turn creates a lot of socio-economic activities which range from mobile shops, cafes, vehicle repairs, vulcanizers, welders, car wash and spare parts dealers. These activities send metals into the air in particulate from and the metals subsequently are deposited into nearby soils which are absorbed by plants on soils (Okunola *et al.* 2008).

In Africa, especially, Nigeria, a high volume of fairly used electronics such as computers and their accessories, TV sets, fax machines, cell phones, etc., are imported into the country, and experts estimated that 25 to 75% of these materials are irreparable junk, and because the country lacks the capacity to safely deal with electronic waste, they wind up in landfills and informal dumps where they decompose and release toxic metals such as lead, cadmium and mercury into the environment; also high levels lead from flaking paint chips from buildings in southern-eastern Nigeria had recently reported (Schmidt 2006; Nduka *et al.* 2008). However, roadside topsoil has become an increasingly important environmental sampling medium for assessing anthropogenic pollutant levels in the urban environment (Wang *et al.* 2005).

Metals, the oldest toxins known to human (Goyer and Clarkson 2001) are known to be persistent environmental pollutants (McAloon and Mason 2003). At elevated levels, essential and non-essential elements are known to cause morphological abnormalities, reduced growth, increased mortality and antigenic effects in humans, plants and animals (Pier and Bang 1980).

The route of exposure to particulate dust and soil metals include inhalation of contaminated particles, direct soil in-

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gestion (usually by children) and ingestion of food produced along the roads (Finzgar *et al.* 2007). Furthermore, paint chips, soil, water, infant formulae, canned and non-canned beverages and paediatric syrup, are chief exposure routes for lead poisoning in children (Maduabuchi *et al.* 2006; Orisakwe and Nduka 2009). The health effects of toxic metals in air and dust from road deposited dust on humans is better appreciated if one consider the fact that an active person typically inhales 10,000 to 20,000 L of air daily (Gbadebo and Bankole 2007).

Cadmium (Cd) is a modern toxic metal (Goyer and Clarkson 2001) usually obtained as a by product from zinc refining (O'Neil 1993). Cd is classed as a cumulative toxin because it has very long body retention, implying that the concentration of Cd in target organ in which Cd has a mean residence of 30 or more years (Elinder *et al.* 1981). A renal cortex concentration of 200 µg/g has been shown to induce renal dysfunction which may be manifested in a variety of ways, the most common of which is proteinuria – the appearance of low molecular weight proteins in the urine (Roels *et al.* 1993). Other effects of Cd in man include kidney damage (Herbert *et al.* 1998), pains in the bone – "itai-itai" disease (Kjellstrem 1986) and endocrine disruption (Schantz and Widholm 2001). Cd also has mutagenic, carcinogenic and tetratogenic effects (Goyer and Clarkson 2001) and toxic to human body at extremely low levels (Okunola *et al.* 2011b). Prolong exposure to the metal results in renal dysfunction, characterized by tubular proteinuria. Exposure to high concentration of Cd leads to obstructive lung disease and Cd pneumonitis, as a result of inhaled dusts and fumes. It is characterized by chest pain, cough with foamy and bloody sputum, and death of the lung tissues' lining because of excessive accumulation of watery fluids (Okunola *et al.* 2011b). Cd is also associated with bone defects such as osteomalacia, osteoporosis and spontaneous fractures, increased blood pressure and myocardic dsyfunctions. Depending on severity of exposure, the symptoms of effects include nausea, vommitting, abdominal cramps, dyspnea and muscular weakness (Okunola *et al.* 2011b). Severe exposure may result inpulmonary odema and death. Pulmonary effects (emphysema, bronchiolitis and aveolitis) and renal effects may occur following subchronic inhalation exposure to cadmium and its compounds (European Union 2002; Young 2005).

Biologically, iron (Fe) plays crucial role in the transport and storage of oxygen, and also in electron transport. It is safe to say that, with only a few possible exceptions in the bacterial world, there would be no life without iron (Greenwood and Earnshaw 1985; Bacha *et al.* 2010); but dissolve ferrous iron gives disagreeable taste (Bacha *et al.* 2010). When the Fe combines with tea, coffee and other beverages, it produce an inky, black, appearance and a harsh unacceptable taste (Bacha *et al.* 2010).

In addition to blood, which contains about 0.5 mg Fe/mL, high concentration of Fe are found in liver and spleen where iron is found in ferritin and hemosiderin. Considerably high values, sometimes exceeding 10 mg/g in liver, have been found in cases of severe hemochromatosis (Bothwell and Bradlow 1960). Documented effects of iron overload are damaged liver, heart, spleen and pancreas (Andrew and Michael 2000). Children afflicted with β-thalassemia major accumulate 4-8 g of Fe/year from transfused blood. The body has no mechanism for excreting such a large amount of Fe and most patient die by age of 20 from toxic effect of Fe overload (Harris 1999). In addition, Fe toxicity accompanies the genetic disease called hereditary hemocromatosis (Wardlaw 2003). For people with this disease, Fe in the body eventually builds up to dangerous amounts, especially in the blood, liver, muscles, pancreas and heart. If not treated, the excess iron deposits contribute to severe organ damage especially in the liver and heart.

Manganese (Mn) is an essential element in the human diet with a normal dietary intake calculated to be approximately 2-5 mg/day (Jankovic 2005). It is a constituent of certain enzymes and can also activate many enzymes (Ogunfowokan *et al.* 2009). The deficiency disorders include spermatogenesis, bone abnormalities, alteration in hair colour loss of weight, sterility, nausea, disorder bleeding, anaemia and lupus eryematosus (Doisy 1973; Hurley 1976). The excess amount of it also causes psychiatric disorder changes in the central nervous system, liver cirrhosis, and irritation in the eyes, testicular damage, lung diseases and hepatic damage, nephritis, hallucination, disturbances of libido and improper coordination (Keen and Zidenberg-Cherr 1993; Kaplan *et al.* 1995; Copeland 1996). Manganese is required for the regulation of reproduction, carbohydrate and lipid metabolism and normal brain function (Keen *et al.* 1999). Severe manganese neurological toxicity (manganism) is related to long term high level exposure to the metal or its inorganic compounds. Neurological symptoms vary and can range from a reduction in general response, irritability, compulsive behaviours, to a Parkinson's –like syndrome. It is important in the processing of biological homeostatic mechanisms, especially those which involve elemental iron (Oyekunle *et al.* 2011)

Lead (Pb) is a highly toxic naturally occurring metal that has always been present in soils, surface waters and ground waters. Pb can cause serious health problems, especially for infants, children and pregnant women (Oyekunle *et al.* 2011). On human beings, Pb has two quite distinctive effects: physiological and neurological. Absorption of lead in the body is enhanced by Calcium (Ca) and Zinc (Zn) deficiencies. Acute and chronic effects of lead results in psychosis (Okunola *et al.* 2011b). Pb poisoning are ill defined symptoms such as nausea, vomiting, abdominal pains, anorexia, constipation, insomnia, anaemia, irritability, mood disturbance and coordination loss (Grandjean and Nielson 1979). In blood, Pb concentrations of less than 10 µg/dL in children and adolescents can cause cognitive defects (Wu *et al.* 2003). Pb effects especially on the foetus and children may include behavioural changes and impaired performance in IQ tests (Fatoki *et al.* 2003). Other health hazard include a reduction in the body immune system, low birth weight, premature birth, reduced sperm count and motility and increased risk of hypertension and birth defects for pregnant women (Adeniyi and Anetor 1999; Ogunfowokan *et al.* 2008).

Zinc (Zn) is an essential element required for life processes of various enzymes (Wordstron 1982). It also interferes at different levels in the endocrine system and lipids and carbohydrate metabolism (Wordstron 1982). Acrodermatitis enterohepatica is a familiar disease characterised by skin eruptions and gastrointestinal disorders as a result of low serum zinc (Schwartz 1975). At elevated level Zn may be carcinogenic (Schwartz 1975). Excessive Zn symptoms include nausea, dizziness, gastric ulcers, lethargy, muscle pain, impairment of immune function, headaches, vomiting, dehydration, stomach-aches, fever, depression, malaisc, cough, poor muscle coordination, fatigue, possible renal failure and increased blood level of insulin-like growth factor and testosterone, both of which are related to prostrate cancer (Michael and Stanford 2003; Bacha *et al.* 2010). Histopathology signs of zinc poisoning, including fibrosis and vacuolization, were associated with elevated pancreatic zinc concentrations (van der Merwe *et al.* 2011).

However, toxicity of Zn is less than that of other heavy metals like Cd, As and Sb (Bacha *et al.* 2010). The Zn deficiency results in retardation of growth, anorexia, lesions of the skin and impaired development and function of reproductive organs (Bacha *et al.* 2010).

Soil chemical properties such as pH, organic matter (OM) and exchangeable cations exerts strong influence on metal availability to plants (Davies 1992; Smith 1996). Soil pH is an important factor that have the ability to control the metal solubility i.e., supply of metals are often adsorbed or precipitated on the surface of carbonates, phosphate and insoluble hydroxide (Kiekens 1984). Metal availability to plants can be reduced by treatments to increase the soil pH. OM is also important to metal solubility in soils (Ge 1999); soil minerals and organic matter effectively reduce the solubility of many trace elements, which allows for application of relatively more than what might be expected if accounting only for short-term plant removal balance (Hopkins and Ellsworth 2005). In addition, it also plays an important role in soil structure, water retention, cation exchange and in the formation of complexes (Alloway and Ayres 1997). The composition of the soil OM is dominated by large molecular weight humin and humic acid compounds and lower molecular weight fulvic acid (Ge 1999). In some cases, organic matter makes a metal more biologically available as it protects it from combining with soil minerals to become mostly insoluble, especially in the case of Zn and Mn. However, Cu is tightly bound by organic matter and, as a result, soil low inorganic matter typically have a much lower tolerance for excessively applied copper (Hopkins and Ellsworth 2005).

The metal–OM interactions affect metal solubility in two ways: OM in the solid phase especially humic compounds of high molecular weight strongly retains metal in soil and this reduces the metal availability to plants (Ross 1994). Secondly, the formation of organometallic compounds in solutions may increase the availability of trace metals to plants as these compounds can enhance the diffusion of metal through the unstirred zone around the plant roots (Chekai *et al.* 1987).

The higher the percentage of sand in the soil, the more likely it is for the soil to have less water and, thereby higher temperatures. High soil temperatures are conducive for degradation of organic matter. Sandy soils tend to have lower organic matter and a much higher susceptibility to copper toxicity (Hopkins and Ellsworth 2005).

Iwo is an ancient semi-urban city with small-scaled industries, such as mechanization of cassava processing, sachet/bottled water production factories, mechanical workshop, and agricultural practices. Recently, there has been a sharp rise in the development of Iwo as evidenced by the establishment of a private University, proliferation of banking industry as well as establishment of telecommunication industries. This has led to an increase in the population of Iwo city, and as a result of this, transportation and traffic flow in and out of Iwo keeps increasing on daily basis. Thus, automobile exhaust, combustion of fossil fuel, poor waste management could rapidly contribute to anthropogenic sources of heavy metals in the Iwo metropolis and its environs.

On the basis of the information above, the chemical speciation of these trace metals from the total metal content in the roadside soil of Iwo was established as it may serve as threat to plants, humans and the environment in general.

MATERIALS AND METHODS

Description of study area

The study was conducted within the city of Iwo, one of the big cities in Osun state, Nigeria. It is located 35 km away from Osogbo (the state capital) on latitude 07° 38′ N and longitude 004° 11′ E. The selected streets are generally associated with daily high traffic density, with petrol stations, market areas, road junctions, shopping malls, automobile workshops and metal works (iron benders and welders) randomly sited along the streets and highways.

Sample collection

Samples were collected in the month of February, 2011 in the morning during the weekend when there were few cars on the roads for safety reasons. Roadside soil was collected from top layer within a depth of 0-5 cm at a distance (about 2-5 m from the edge of the road) where there were no intervening pavements at the sampling locations. Extraneous substances such as dead leaves and stones were carefully removed from the soil. About 200 g of soil was collected from five sub-samples from each sample location using a clean stainless hand auger. The stainless auger was washed with dilute nitric acid solution and thereafter rinsed with deionised water and dried between sample collections in order to avoid cross contamination. The collected soil samples at a site were pooled together as a composite representative sample and air-dried at ambient temperatures to a constant weight on an aluminium foil placed in a fairly aerated cupboard to further prevent cross contamination. The air-dried soil samples were sieved with a 2 mm stainless steel sieve to remove large materials. The sieved samples were pulverized using an agate mortar and pestle.

Apparatus and reagent used

All glassware, polypropylene tubes and Teflon beakers used were first washed with detergents, rinsed with tap water and distilled water, and then soaked in 10% HNO_3 (v/v) for 48 h (Ogunfowokan *et al.* 2009). They were then re-washed with detergent and rinsed thoroughly with doubly distilled water. Afterward, the apparatus were oven dried for 12 h at a temperature of 80°C. The entire reagent used, viz. HCl, HNO_3 and NH_4COOCH_3 (Park Scientific Ltd., Northampton, UK); H_2SO_4 and $NH_2OH.HCl$ (BDH Laboratory Supplies, Poole, UK); $(NH_4)_2C_2O_4$ (Merck, Kennzechung, Germany); H_2O_2 (Philip Harris Ltd., Birmingham, UK); $HClO_4$ (ES 5, Nottingham, England); CH_3COOH and NH_4COOCH_3 (M&B Ltd., Dagenham, UK) and CH_3COONa (Sigma-Aldrich Pty Ltd., Pretoria, South Africa).

Electrical conductivity and pH

Electrical conductivity (Ec) and pH were measured with a soil: water ratio of 1:2 (Hendershot *et al.* 1993) using pH Testr waterproof digital pH meter and EC Testr 2 model dual range water proof digital EC meter.

Organic matter

OM was determined by ashing 0.5 g of soil sample in a Vecstar Muffle furnace model ECF 3 at 500°C for 1 h. The loss in weight of the residue gave the OM in the sample.

Carbonate

A 0.5 g finely divided soil was placed in a 25 mL of distilled water. The solution was titrated with 0.01 M HCl using methyl red indicator. The carbonate content was calculated as the $CaCO_3$ total alkalinity.

Determination of total metal

Since no soil standard reference material was available to us at the time of this study, 1 g of each sample was acid digested using the method described elsewhere (Ogunfowokan *et al.* 2009). The levels of total metals were determined and compared with the sum of the fractions in each sample to establish the closeness, and hence, the degree of accuracy of the results obtained.

Sequential extraction procedure

The procedure of Tessier *et al.* (1979, 1985) was used for this study except for the introduction of two important factors (water soluble and plant available). In this scheme, trace elements were separated into nine operationally defined fractions: water soluble (F1), exchangeable (F2), bound to carbonate (F3), plant available (F4), bound to Mn (F5), bound to amorphous Fe oxide (F6), bound to crystalline oxide (F7), bound to OM (F8), and residual fraction (F9).

From the pulverized sample selected by coning and quartering, 1 g of dust sample was weighed and extractions were made through steps (F) by centrifugation and filtration at 10,000 rpm placing the sample in centrifuge tube. Deionised water was used to wash the residues following subsequent extractions in order to ensure selective dissolution and avoid possible inter-phase mixing between the extractants. All samples were run in triplicates.

Water soluble metals (F1): Water soluble metals were extracted with a solution of 25 mL doubly distilled water at pH 7.0 and at 28°C for 2 h

Exchangeable metals (F2): The residue from (F1) was extracted with 25 mL of 1.0 M NH_4COOCH_3 (pH 7). The suspension

Table 1 Geographical locations (GPS grid coordinates) of the sampling sites.

Location	N-Coordinate	E-Coordinate	Elevation (m)	Traffic volume count/h
Hospital Road	07° 37′ 776″	004° 11′ 489″	240.18	483
Water works	07° 38′ 468″	004° 11′ 827″	245.97	448
Osogbo Road	07° 39′ 296″	004° 12′ 321″	262.13	453
Ejigbo Road	07° 39′ 541″	004° 11′ 266″	245.36	312
Odo-Ori market	07° 39′ 267″	004° 11′ 305″	256.03	1197
Ibadan Road	07° 38′ 513″	004° 09′ 946″	244.14	357
Adeke Road	07° 07′ 680″	004° 09′ 562″	234.70	522
Bowen University. Road	07° 07′ 465″	004° 11′ 286″	242.32	841
Agbowo Estate	07° 39′ 727″	004° 11′ 013′	257.86	Nd

was shaken for 30 min at 28°C.

Metals bound to carbonate (F3): The residue from (F2) was extracted with 3 M sodium acetate ($CH_3COO^-Na^+$) adjusted to pH 5.0 with acetic acid (CH_3COOH). The suspension was shaken for 5 h.

Plant available metals (F4): The residue from (F3) was extracted by shaking with a solution mixture of 25 mL of 0.025 M HCI + 0.05 M H_2SO_4 for 30 min at 28°C.

Bound to Mn-Oxide (F5): The residue from (F4) was shaken for 30 min at 28 °C with a solution of 25 mL 0.1 M $NH_2OH.HCl$ in 25% CH_3COOH (pH 2-3).

Bound to amorphous Fe-oxide (F6): The residue from (F5) was extracted with 25 mL of 0.2 M $(NH4)_2C_2O_4$ (pH 3) for 30 min at 50°C using a water bath with occasional stirring.

Bound to crystalline Fe-oxide (F7): The residue from (F6) was extracted using 25 mL of 0.04 M $NH_2OH.HCI$ in 25 % acetic acid (pH 2) and heated in a water bath with occasional stirring at 100°C for 6 h.

Bound to OM (F8): The residue from (F7) was extracted with 10 mL of 0.02M HNO_3 and 15 mL of 30% H_2O_2 (adjusted to pH 2 with HNO_3). The mixture was then heated to 85^oC for 5 h with occasional agitation. A second 15 mL aliquot of 30% (pH 2 with HNO_3) was added and the mixture heated again to 85^oC for 3 h with intermittent agitation. After cooling, 5 mL of 3.2 M NH_4COOCH_3 in 20% (v/v) HNO_3 was added and the samples diluted to 20 mL and agitated continuously for 30 min.

Residual metals (F9): The residue from (F8) was digested with a 3:1 mixture of concentrated HNO_3 and $HClO_4$ for 8 h.

QUALITY CONTROL MEASURES

Recovery analysis

For sediment analysis, a 1 g sediment samples was put in Teflon in the presence of 6 mL HNO_3 acid. This was spiked with 25 mL of 50 µg/mL of the metals and digested using the method already described. The digested spiked sample was made up to mark in a 25 mL volumetric flask with doubly distilled water. The resulting solutions were taking for AAS analysis. The results obtained were compared with those of the spiked water and sediment samples to obtain the recovery analysis. Duplicate analysis was carried out to further check the reproducibility of the methods used in this study. The percentage recovery (% R) for each metal was calculated using the relationship:

$$\% R = \frac{A - B}{C} \times 100$$

where A = concentration of a metal in the spiked sample; B = concentration of a metal in the unspiked sample; and C = the amount of metal (ppm) used for spiking.

Quantification process

The metal content of all the extracts in the centrifuged and digested solutions were determined using Buck Model 205 Flame Atomic Absorption Spectrophotometer, East Norwalk, United State of America available at the International Institute of Tropical Agricultural (IITA), Ibadan, Nigeria.

Mobility factor (MF) determination

The MF, an index of potential mobility of metal ions in soil [Narwal and Singh 1998; Salbu *et al.* 1998], was determined on the basis of the absolute and relative values of fractions (F1, F2, F3 and F4) weakly bound to soil components using the relationship:

$$MF = \frac{F1 + F2 + F3 + F4}{F1 + F2 + ... + F9} \times 100$$

Statistical analysis of data

The mean standard deviation for the trace metals and physicochemical parameters from three replicate measurements were determined using the statistical package for social sciences (SPSS) software, 15.0 for window evaluation version. General subsequent evaluation of the data was done using the mean values. The linear correlation coefficient of the physico-chemical parameters and trace metals were determined using the Pearson correlation coefficient. The dependence of trace metal concentrations on traffic density was evaluated by calculation of the Spearman rank correlation coefficient.

RESULTS AND DISCUSSION

Table 1 gives the geographical locations of the sampling site. The study area lies within longitudes 4° 9′ 562″ to 4° 12′ 321″ E and latitudes 7° 7′ 465″ to 7° 39′ 776″ N, while the land elevation is within 234.70 m and 262.13 m above sea level. The traffic volume count was between 312 and 1197 vehicles per h.

Table 2 contains the results of the recovery analyses conducted. Under the experimental conditions used, the standard calibration curves obtained showed high linearity level with r^2 values between 0.9253 for Mn and 0.9952 for Fe. Recoveries of heavy metals in soil ranged from 89.79% for Cd to 98.66% for Zn. These values are adjudged acceptable, and hence, the results obtained are reliable.

The physicochemical parameters in the roadside soil of Iwo are presented in **Table 3**. The pH values for the roadside soil range from 7.90-11.60 with mean value of 9.11 ± 1.20. This shows that the soil is alkaline in nature. The soil conductivity range between 230 to 280 µS/cm with mean value of 250.56 ± 17.76 µS/cm. The $CaCO_3$ range between 40 to 84 mg/L with mean value of 56.22 ± 14.88 mg/L. The percentage OM range between 2 to 62% with mean value of 17.63 ± 20.64%. The high percentage OM was obtained in Bowen road.

Table 2 Calibration curve and percentage recovery (% R) for trace metals.

Trace Metals	Calibration curve, r^2	% Recovery*
Mn	0.9253	91.21 ± 5.31
Fe	0.9952	95.39 ± 5.60
Zn	0.9698	98.66 ± 3.06
Cd	0.9819	89.79 ± 4.35
Pb	0.9891	95.39 ± 3.86

*Values are mean of triplicate analysis ± % RSD

Table 3 The physicochemical parameters of roadside soils of Iwo.

	pH	Conductivity (µS/cm)	$CaCO_3$ (mg/L)	Organic matter (%)
Mean ± SD	9.11 ± 1.20	250.56 ± 17.76	56.22 ± 14.88	17.73 ± 20.64
Range	7.90-11.60	230-280	40-84	02-62

Table 4 Total metal levels in the roadside soil of Iwo.

	Mn	Pb	Cd	Fe	Zn
Adeeke	121.02 ± 1.30	0.79 ± 0.00	0.38 ± 0.00	192.48 ± 1.75	56.24 ± 0.77
Agbowo	107.50 ± 2.05	0.89 ± 0.02	0.43 ± 0.01	183.50 ± 2.70	52.95 ± 1.32
Bowen	95.48 ± 2.15	0.91 ± 0.02	0.40 ± 0.01	159.65 ± 1.55	51.59 ± 1.78
Ejigbo	100.55 ± 1.98	0.91 ± 0.01	0.39 ± 0.00	163.34 ± 1.89	51.25 ± 1.65
Express	90.75 ± 1.47	0.97 ± 0.02	0.45 ± 0.01	168.15 ± 1.98	50.70 ± 0.92
Hospital	104.39 ± 1.70	0.80 ± 0.01	0.36 ± 0.00	176.90 ± 16.85	52.87 ± 1.40
Odo-Ori	98.46 ± 1.27	0.93 ± 0.02	0.46 ± 0.01	168.55 ± 1.96	46.89 ± 1.05
Osogbo	118.53 ± 1.62	0.95 ± 0.01	0.44 ± 0.00	183.68 ± 2.77	52.80 ± 1.08
Waterworks	103.99 ± 22.86	0.90 ± 0.01	0.40 ± 0.00	160.75 ± 1.98	49.47 ± 0.85
Mean ± SD	104.52 ± 10.01	0.89 ± 0.06	0.41 ± 0.03	173.00 ± 11.64	51.64 ± 2.60

Total metal concentrations

The total trace metal levels in the roadside soil from each site reflect varied degrees of contamination, as presented in **Table 3**. The values of Mn ranged from 90.75 ± 1.47 and 121.02 ± 1.30 µg/g, yielding an overall mean of 104.52 ± 10.01 µg/g; Pb ranged from 0.79 ± 0.00 and 0.97 ± 0.02 µg/g yielding an overall mean of 0.89 ± 0.06 µg/g; Cd ranged from 0.36 ± 0.00 and 0.46 ± 0.01 µg/g with overall mean of 0.41 ± 0.03; Fe ranged from 159.65 ± 1.55 and 192.48 ± 1.75 µg/g, yielding an overall mean of 173.00 ± 11.64 µg/g; and Zn ranged from 46.89 ± 1.05 and 56.24 ± 0.77 µg/g, yielding overall mean of 51.64 ± 2.60 µg/g. In general, the highest level of Mn (121.02 ± 1.30 µg/g) correspond to the sample from Adeeke, with traffic volume count of 522 vehicles h^{-1}; Pb has the highest level of (0.97 ± 0.02 µg/g) correspond to the sample from Ibadan express road with traffic volume count of 357 vehicles h^{-1}; Cd has the highest levels of (0.46 ± 0.01 µg/g) correspond to the sample from Odo-ori with traffic count volume of 1197 vehicles h^{-1}; Fe and Zn have the highest levels of (192.48 ± 1.75 µg/g), (56.24 ± 0.77 µg/g) respectively correspond to the sample from Adeeke with traffic volume count of 522 vehicles h^{-1} (**Tables 1, 4**).

The mean level of Mn obtained in this study (104.52 ± 10.01) is higher than the value of street dust (51.46 ± 15.10 µg/g) reported by Ogunfowokan *et al.* (2009). Furthermore, the range and mean levels of Mn reported for Tshwane, South Africa soil (215.2-920.5 µg/g) Moja (2007), Bangalore soil (205.8 µg/g), Spanish soil (366-1815 µg/g), and for Ghana (233 – 1240 µg/g) (Addo *et al.* 2012) are much higher than those of our findings in this study. Tyre wear and brake lining may have contributed to the manganese concentrations obtained in this study because manganese and other metals have been reported to be present in motor vehicles (Ondov 1974). Before the progressive and eventual total elimination of lead from Nigerian premium motor spirit (PMS) is estimated to contain about 0.7 g of lead added as anti-knock tetra ethyl lead, which amounted to about 24.5 tonnes of Pb being released into Nigerian environment everyday (Ojo *et al.* 2010). This data is evidence of the compliance of the petrochemical industry in Nigeria to produce non-leaded fuel. Despite the fact that the levels of Pb in this study area were generally low but higher in areas with relatively high traffic volume, the levels obtained in this study (0.79 ± 0.00 to 0.97 ± 0.02 µg/g) were lower than those reported by Ogunfowokan *et al.* (2004, 2009) (196.8 ± 0.04 to 108 ± 0.03 µg/g; 22.23 ± 3.52 to 43.48 ± 3.05 µg/g) in Ile-Ife, monitoring local atmosphere pollution of the south-western city of Nigeria. In a similar manner, the levels were lower than that reported for other urban cities in Nigeria such as Osogbo (9.8-136.1 µg/g) by Fakayode and Olu-Owolabi (2003), Ibadan (81 ± 140 µg/g) by Onianwa (2001), Port-Harcourt (15.9-169.5 µg/g) by Ideriah *et al.* (2004), Onitsha (120 ± 0.00 and 80.36 ± 0.00 mg/kg), Nnewi (33.40 ± 0.01 and 4238.29 ± 0.00 mg/kg), Aba (22.56 ± 0.01 and 21.28 ± 0.00 mg/kg) by Nduka and Orisakwe (2010), Minna and Biba (64 ± 17, 43 ± 42 mg/kg) by Iyaka and Kakulu (2011), and Abuja (281 ± 39 mg/kg) by Kakulu (2003). The mean level of Pb recorded in this study were lower than those reported of roadside soil from other countries such as Michigan (12-22 mg/kg) by Howard and Sova (1993), Damascus, Syria (78.4-832 µg/g) by Othman *et al.* (1997), Brisbane, Australia (2910 ± 660 µg/g) by Al-Chalabi and Hawker (2000), Bangalore, India (70-280.5 µg/g) by Ramakrishnaiah and Somashekar (2002), Vilnius-Klaipeda, Lithuania (7.88-54.27 mg/kg) by Grigallaviciene *et al.* (2005), Agra, India (0.00-50.10 mg/kg) by Shashank and Prasad (2010), and Ghana (3.1-67.8 µg/g) by Addo *et al.* (2012). The reasons for the higher levels of lead reported for other countries compared to Iwo are likely to be due to urbanization, industrialization and higher automobile exhaust due to higher traffic volume reported of the former. The background soil Pb contents varied widely; hence, there is no universally accepted safe level (Iyaka and Kakulu 2011). However, the average levels reported in literatures for background Pb total concentrations by various research authors include 10 ppm (Alloway 1990), 15 ppm (Berrow and Reaves 1984), 19 ppm (Brady 1984), 20 ppm (Andriano 1986; Ward 1995) and 29.2 ppm (Fergusson 1990). In this study, the Pb concentrations were lower than these background levels. The elimination of tetraethyl lead from Nigeria gasoline and low industrialization of Iwo might be the likely cause of low level of Pb in the soil. The mean level of Cd (0.41 ± 0.03 µg/g) from this study is lower when compared with (0.55 ± 0.49) of Ibadan soil reported by Onianwa (2001); and Abuja (66 ± 23 mg/kg) by Kakulu (2003) .The level of Cd reported in this study were higher than those reported of roadside soil from other countries viz. Lithuania (0.096-1.19 mg/kg), but lower than Bangalore (21.10 µg/g) and Agra, India (0.00-21.53 mg/kg). However, the level of Cd obtained in this study was above the literature levels (0.35 ppm) of typical soil (Brady 1984). Monaci *et al.* (2000) noted that Cd is associated with motor traffic emission as constituent of motor alloys or with the electronic components and batteries of cars. As a result of impurities in Zn materials, Cd also accompanies ZnO used in tyre manufacture.

The mean level of Fe (173.00 ± 11.64 µg/g) might be from body rust of most vehicles and engine parts. The mean level of Zn (51.64 ± 2.60 µg/g) from this study was higher than results obtained from Ibadan soil (48 ± 37 µg/g) reported by Onianwa (2001), Osogbo soil (42.45 ± 17.68) reported by Fakayode and Olu-Owolabi (2003), Bida soil (38 ± 22 mg/kg) by Iyaka and Kakulu (2011), and Port-Harcourt soil (40.10 ± 15.86 µg/g) reported by Ideriah *et al.* (2004). The mean level of Zn from this study was lower than Minna soil (69 ± 34 mg/kg) reported by Iyaka and Kakulu (2011) and Bangalore soil (176.4 µg/g) reported by Ramakrishnaiah and Somashekar (2002) but higher than 40 ppm

Table 5 Mn levels in different fractions of roadside soil of selected roads of Iwo.

	Water-soluble (F1)	**Exchangeable**	**Carbonate bound**	**Plant Available**	**Mn-Oxide bound**
Adeeke	8.03 ± 0.06	11.87 ± 0.19	13.00 ± 0.16	15.15 ± 0.25	19.00 ± 0.18
Agbowo	10.10 ± 0.25	11.35 ± 0.19	12.01 ± 0.05	11.37 ± 0.20	15.44 ± 0.12
Bowen	11.20 ± 0.24	9.93 ± 0.26	7.05 ± 0.10	14.04 ± 0.17	10.93 ± 0.17
Ejigbo	10.10 ± 0.12	8.68 ± 0.52	9.44 ± 0.13	10.01 ± 0.18	21.07 ± 0.13
Express	9.81 ± 0.08	11.10 ± 0.16	10.10 ± 0.30	9.54 ± 0.26	7.88 ± 0.21
Hospital	10.40 ± 0.09	13.08 ± 0.14	12.09 ± 0.14	11.03 ± 0.08	17.13 ± 0.27
Odo-Ori	10.56 ± 0.14	10.48 ± 0.14	14.09 ± 0.15	8.06 ± 0.11	8.44 ± 0.09
Osogbo	12.25 ± 0.20	11.01 ± 0.04	8.90 ± 0.25	13.09 ± 0.14	13.03 ± 0.08
Waterworks	11.00 ± 0.21	10.44 ± 0.13	13.10 ± 0.15	9.93 ± 0.27	10.89 ± 0.22
Mean ± SD	10.36 ± 1.12	10.71 ± 1.36	11.09 ± 2.26	11.36 ± 2.25	13.76 ± 4.53

	Amorphous Fe-Oxide bound	**Crystalline Fe-Oxide bound**	**Organic matter**	**Residual**	**Total**
Adeeke	12.29 ± 0.13	17.43 ± 0.15	14.43 ± 0.15	11.06 ± 0.13	122.26 ± 1.40
Agbowo	9.91 ± 0.19	9.12 ± 0.19	19.57 ± 0.62	8.59 ± 0.22	107.46 ± 2.03
Bowen	15.59 ± 0.55	10.06 ± 0.27	8.93 ± 0.39	8.06 ± 0.11	95.79 ± 2.26
Ejigbo	13.88 ± 0.20	8.37 ± 0.54	9.40 ± 0.12	8.84 ± 0.47	99.79 ± 1.94
Express	7.49 ± 0.15	15.03 ± 0.14	10.45 ± 0.09	10.43 ± 0.13	91.83 ± 1.52
Hospital	10.96 ± 0.19	10.82 ± 0.33	10.11 ± 0.17	9.46 ± 0.09	105.08 ± 1.50
Odo-Ori	10.02 ± 0.05	11.41 ± 0.15	8.04 ± 0.13	15.87 ± 0.21	96.97 ± 0.96
Osogbo	14.16 ± 0.24	14.97 ± 0.34	20.99 ± 0.14	9.42 ± 0.14	117.82 ± 1.57
Waterworks	9.94 ± 0.13	14.49 ± 0.16	17.03 ± 0.41	7.84 ± 0.25	104.44 ± 24.26
Mean ± SD	11.58 ± 2.52	12.41 ± 3.06	13.22 ± 4.78	9.95 ± 2.38	104.60

Table 6 Zn levels in different fractions of roadside soil of selected roads of Iwo.

	Water-soluble (F1)	**Exchangeable**	**Carbonate bound**	**Plant Available**	**Mn-Oxide bound**
Adeeke	5.11 ± 0.15	5.95 ± 0.09	6.33 ± 0.15	6.99 ± 0.03	5.99 ± 0.02
Agbowo	6.09 ± 0.15	5.65 ± 0.19	4.99 ± 0.02	6.45 ± 0.10	5.89 ± 0.20
Bowen	5.17 ± 0.28	6.32 ± 0.15	4.68 ± 0.16	6.29 ± 0.15	5.96 ± 0.25
Ejigbo	4.87 ± 0.19	6.89 ± 0.16	5.22 ± 0.19	6.00 ± 0.03	6.98 ± 0.04
Express	4.00 ± 0.04	8.04 ± 0.08	4.94 ± 0.11	5.20 ± 0.09	5.00 ± 0.01
Hospital	5.12 ± 0.16	6.32 ± 0.10	6.09 ± 0.13	6.08 ± 0.13	5.87 ± 0.20
Odo-Ori	4.31 ± 0.10	4.49 ± 0.10	6.21 ± 0.16	4.43 ± 0.08	5.25 ± 0.07
Osogbo	5.14 ± 0.10	6.08 ± 0.12	5.26 ± 0.09	7.03 ± 0.18	4.28 ± 0.12
Waterworks	6.62 ± 0.13	4.99 ± 0.02	5.72 ± 0.15	6.32 ± 0.02	4.01 ± 0.01
Mean ± SD	5.16 ± 0.79	6.25 ± 0.82	5.50 ± 0.60	6.09 ± 0.81	5.47 ± 0.91

	Amorphous Fe-Oxide bound	**Crystalline Fe-Oxide bound**	**Organic matter**	**Residual**	**Total**
Adeeke	5.83 ± 0.15	6.01 ± 0.03	7.92 ± 0.14	5.98 ± 0.03	56.11 ± 0.76
Agbowo	5.16 ± 0.13	5.22 ± 0.14	7.14 ± 0.22	5.26 ± 0.09	51.85 ± 1.25
Bowen	6.25 ± 0.16	5.88 ± 0.20	5.95 ± 0.25	4.87 ± 0.16	51.37 ± 1.72
Ejigbo	4.99 ± 0.05	5.44 ± 0.17	6.03 ± 0.06	5.36 ± 0.09	51.78 ± 1.75
Express	4.27 ± 0.16	6.83 ± 0.17	6.14 ± 0.09	5.43 ± 0.15	49.85 ± 0.90
Hospital	5.33 ± 0.20	6.26 ± 0.09	6.87 ± 0.20	5.63 ± 0.15	53.57 ± 1.38
Odo-Ori	4.93 ± 0.27	6.00 ± 0.03	5.00 ± 0.02	6.06 ± 0.18	46.68 ± 1.01
Osogbo	6.08 ± 0.13	5.99 ± 0.12	7.09 ± 0.14	6.20 ± 0.09	53.15 ± 1.06
Waterworks	5.41 ± 0.11	5.00 ± 0.19	6.66 ± 0.20	4.99 ± 0.02	49.72 ± 0.87
Mean ± SD	5.36 ± 0.61	5.85 ± 0.55	6.53 ± 0.84	5.53 ± 0.46	51.56

reported by Berrow and Reaves (1984) for world soil. Some lubricating oil contains important additives such as antioxidant Zn dithiophosphate as well as tyres of motor vehicle (Lagerweff and Specht 1970). This might be the reason for high levels of Zn recorded in this study. With exception of Cd, the analytical results indicate that the levels of trace metals studied were below the literature levels of a typical soil.

Despite the fact that total metal content of polluted metals in the soil can be useful for the characterization of contamination intensity, the speciation of trace metals with selective extracting agents gives further information about the fundamental reactions that govern the behaviour of metals in the soil (Olajire *et al*. 2003). In this study, results of speciation analysis of Mn in the samples (**Table 5**) gave the overall mean amount of Mn in the following decreasing order: Mn-Oxide bound > OM > Crystalline Fe-oxide > amorphous Fe-Oxide > plant available > carbonate bound > exchangeable > water soluble > residual. **Table 6** shows the results of speciation analysis of Zn in the sample which gave the overall mean amount of Zn in the following decreasing order: OM > exchangeable > plant available > crystalline Fe-oxide > residual > carbonate > Mn-oxide > amorphous Fe-oxide > water soluble. **Table 7** and **8** gave the results of speciation analysis of Pb and Cd in which the overall mean of these metals were almost similar. **Table 9** gave the results of speciation analysis of Fe in which the overall mean amount of Fe was in the following decreasing order: Mn-Oxide > OM > plant available > armorphous Fe-oxide > crystalline Fe-oxide > exchangeable = carbonate > residual > water soluble. In this study, most of Mn, Zn and Fe resided in the Mn-oxide and OM fractions. This might be due to the alkaline nature of the soil. Ge (1999) reported that as the soil solution becomes more alkaline, the more metals form complexes with OH^-, CO_3^- and HCO_3^-. Furthermore, some metals such as Fe and Cu have a strong tendency to form soluble compound with oxygen-containing functional groups of dissolved OM. Moreover, the dissolution of soil OM is enhanced at neutral or alkaline pH and therefore more dissolved metals are organically complexed. In addition to this, at low level of dissolved metals, adsorption of metal ions into oxide and OM may control the metal solubility (Ge 1999). When the metal loadings are high and the soil is alkaline, precipitation processes may begin to control the concentrations of metal in the soil solution (McBride 1989). The high level of Mn in the organic bound

Table 7 Pb levels in different fractions of roadside soil of selected roads of Iwo.

	Water-soluble (F1)	Exchangeable	Carbonate bound	Plant Available	Mn-Oxide bound	Amorphous Fe-Oxide bound	Crystalline Fe-Oxide bound	Organic matter	Residual	Total
Adeeke	0.09 ± 0.00	0.09 ± 0.00	0.08 ± 0.00	0.09 ± 0.00	0.10 ± 0.00	0.09 ± 0.00	0.09 ± 0.00	0.10 ± 0.00	0.08 ± 0.00	0.81 ± 0.00
Agbowo	0.10 ± 0.00	0.09 ± 0.00	0.10 ± 0.00	0.10 ± 0.01	0.11 ± 0.01	0.09 ± 0.00	0.10 ± 0.00	0.09 ± 0.00	0.09 ± 0.00	0.87 ± 0.02
Bowen	0.10 ± 0.00	0.11 ± 0.00	0.10 ± 0.00	0.10 ± 0.01	0.11 ± 0.01	0.10 ± 0.01	0.11 ± 0.01	0.12 ± 0.01	0.09 ± 0.00	0.94 ± 0.03
Ejigbo	0.11 ± 0.00	0.11 ± 0.01	0.09 ± 0.00	0.10 ± 0.00	0.10 ± 0.01	0.09 ± 0.00	0.09 ± 0.00	0.10 ± 0.00	0.10 ± 0.00	0.89 ± 0.01
Express	0.10 ± 0.00	0.12 ± 0.00	0.09 ± 0.00	0.09 ± 0.00	0.10 ± 0.00	0.11 ± 0.01	0.10 ± 0.00	0.11 ± 0.01	0.10 ± 0.00	0.92 ± 0.02
Hospital	0.09 ± 0.01	0.09 ± 0.00	0.08 ± 0.00	0.09 ± 0.00	0.09 ± 0.00	0.11 ± 0.01	0.09 ± 0.00	0.09 ± 0.00	0.09 ± 0.00	0.82 ± 0.01
Odo-Ori	0.10 ± 0.00	0.10 ± 0.00	0.11 ± 0.00	0.08 ± 0.00	0.10 ± 0.00	0.10 ± 0.01	0.11 ± 0.01	0.10 ± 0.01	0.10 ± 0.00	0.90 ± 0.02
Osogbo	0.12 ± 0.00	0.10 ± 0.00	0.10 ± 0.00	0.11 ± 0.00	0.10 ± 0.00	0.10 ± 0.00	0.08 ± 0.01	0.10 ± 0.00	0.13 ± 0.01	0.94 ± 0.01
Waterworks	0.09 ± 0.00	0.11 ± 0.00	0.09 ± 0.00	0.10 ± 0.00	0.10 ± 0.00	0.11 ± 0.00	0.09 ± 0.00	0.11 ± 0.01	0.11 ± 0.01	0.91 ± 0.01
Mean ± SD	0.10 ± 0.01	0.11 ± 0.01	0.10 ± 0.01	0.10 ± 0.01	0.10 ± 0.01	0.10 ± 0.01	0.10 ± 0.01	0.10 ± 0.01	0.10 ± 0.01	0.89

Table 8 Cd levels in different fractions of roadside soil of selected roads of Iwo.

	Water-soluble (F1)	Exchangeable	Carbonate bound	Plant Available	Mn-Oxide bound	Amorphous Fe-Oxide bound	Crystalline Fe-Oxide bound	Organic matter	Residual	Total
Adeeke	0.04 ± 0.01	0.04 ± 0.00	0.04 ± 0.00	0.04 ± 0.00	0.04 ± 0.00	0.04 ± 0.00	0.04 ± 0.00	0.05 ± 0.00	0.04 ± 0.00	0.37 ± 0.00
Agbowo	0.05 ± 0.00	0.05 ± 0.01	0.05 ± 0.00	0.04 ± 0.00	0.05 ± 0.00	0.04 ± 0.00	0.05 ± 0.00	0.04 ± 0.00	0.04 ± 0.00	0.41 ± 0.01
Bowen	0.05 ± 0.00	0.04 ± 0.00	0.05 ± 0.01	0.04 ± 0.00	0.04 ± 0.00	0.05 ± 0.00	0.05 ± 0.00	0.05 ± 0.00	0.04 ± 0.00	0.41 ± 0.01
Ejigbo	0.06 ± 0.00	0.05 ± 0.00	0.04 ± 0.00	0.05 ± 0.00	0.05 ± 0.00	0.04 ± 0.00	0.03 ± 0.00	0.04 ± 0.00	0.05 ± 0.00	0.41 ± 0.00
Express	0.05 ± 0.00	0.04 ± 0.01	0.05 ± 0.00	0.04 ± 0.00	0.04 ± 0.00	0.05 ± 0.00	0.05 ± 0.00	0.05 ± 0.00	0.04 ± 0.00	0.41 ± 0.01
Hospital	0.03 ± 0.00	0.04 ± 0.00	0.03 ± 0.00	0.04 ± 0.00	0.04 ± 0.00	0.05 ± 0.00	0.04 ± 0.00	0.04 ± 0.00	0.04 ± 0.00	0.35 ± 0.00
Odo-Ori	0.05 ± 0.00	0.05 ± 0.00	0.05 ± 0.00	0.04 ± 0.00	0.04 ± 0.00	0.05 ± 0.00	0.05 ± 0.00	0.05 ± 0.00	0.04 ± 0.00	0.42 ± 0.00
Osogbo	0.05 ± 0.00	0.05 ± 0.00	0.04 ± 0.00	0.05 ± 0.00	0.04 ± 0.00	0.05 ± 0.00	0.04 ± 0.00	0.05 ± 0.00	0.05 ± 0.00	0.42 ± 0.00
Waterworks	0.04 ± 0.00	0.04 ± 0.01	0.04 ± 0.00	0.05 ± 0.00	0.05 ± 0.00	0.05 ± 0.00	0.05 ± 0.00	0.05 ± 0.00	0.05 ± 0.00	0.42 ± 0.00
Mean ± SD	0.05 ± 0.01	0.04 ± 0.01	0.04 ± 0.01	0.04 ± 0.01	0.04 ± 0.01	0.05 ± 0.01	0.05 ± 0.01	0.05 ± 0.01	0.04 ± 0.01	0.40

Table 9 Fe levels in different fractions of roadside soil of selected roads of Iwo.

	Water-soluble (F1)	Exchangeable	Carbonate bound	Plant available	Mn-Oxide bound	Amorphous Fe-Oxide bound	Crystalline Fe-Oxide bound	Organic matter	Residual	Total
Adeeke	13.03 ± 0.20	20.09 ± 0.10	21.98 ± 0.10	24.87 ± 0.20	24.52 ± 0.28	20.05 ± 0.09	22.66 ± 0.12	23.07 ± 0.33	22.94 ± 0.30	193.18 ± 1.60
Agbowo	19.93 ± 0.10	17.14 ± 0.25	17.14 ± 0.25	24.01 ± 0.48	24.15 ± 0.25	17.96 ± 0.14	16.15 ± 0.54	29.16 ± 0.27	16.96 ± 0.23	182.60 ± 2.53
Bowen	20.03 ± 0.07	15.19 ± 0.27	15.19 ± 0.27	21.94 ± 0.10	21.07 ± 0.13	24.04 ± 0.21	14.07 ± 0.21	14.88 ± 0.21	14.04 ± 0.42	160.45 ± 1.85
Ejigbo	16.10 ± 0.16	18.15 ± 0.24	18.15 ± 0.24	20.09 ± 0.16	27.99 ± 0.23	16.87 ± 0.20	12.90 ± 0.15	18.08 ± 0.17	14.08 ± 0.34	162.41 ± 1.91
Express	17.08 ± 0.33	17.03 ± 0.12	17.03 ± 0.12	15.96 ± 0.33	16.04 ± 0.09	13.40 ± 0.15	29.67 ± 0.16	20.97 ± 0.26	19.25 ± 0.38	166.43 ± 1.92
Hospital	17.43 ± 0.14	19.50 ± 2.48	19.50 ± 2.48	22.22 ± 0.21	21.77 ± 0.30	21.99 ± 0.01	12.52 ± 11.92	20.97 ± 0.17	19.93 ± 0.12	175.83 ± 15.80
Odo-Ori	21.06 ± 0.11	22.97 ± 0.15	22.97 ± 0.15	12.95 ± 0.13	16.97 ± 0.24	17.07 ± 0.17	21.13 ± 0.37	13.08 ± 0.15	22.60 ± 0.58	170.80 ± 2.01
Osogbo	19.02 ± 0.33	16.02 ± 0.07	16.02 ± 0.07	21.24 ± 0.54	19.84 ± 0.39	21.97 ± 0.16	21.99 ± 0.03	25.05 ± 0.38	21.12 ± 0.56	182.45 ± 2.50
Waterworks	21.04 ± 0.42	20.89 ± 0.20	20.89 ± 0.20	20.99 ± 0.02	18.80 ± 0.41	17.16 ± 0.25	20.00 ± 0.02	22.72 ± 0.18	16.11 ± 0.30	160.60 ± 2.00
Mean ± SD	18.30 ± 2.58	18.77 ± 2.71	18.77 ± 2.71	20.48 ± 3.68	21.24 ± 3.74	18.95 ± 3.23	18.90 ± 6.15	20.89 ± 4.84	18.56 ± 3.33	172.75

Table 10 Value of mobility factor (MF) of trace metals in soil of Iwo.

	Mn	Pb	Cd	Fe	Zn
Adeeke	39.30	43.21	43.24	41.40	43.45
Agbowo	41.72	44.83	46.34	42.84	44.71
Bowen	44.08	43.62	43.90	45.09	43.72
Ejigbo	38.31	46.07	48.78	44.63	44.38
Express	44.16	43.48	43.90	40.32	44.49
Hospital	44.35	42.68	37.84	44.73	44.07
Odo-Ori	42.48	43.33	45.24	35.09	41.65
Osogbo	38.41	45.74	45.24	39.63	44.23
Waterworks	42.49	47.25	40.48	52.19	47.57
Mean ± SD	41.70 ± 2.45	44.67 ± 1.57	43.88 ± 3.21	42.88 ± 4.72	44.25 ± 1.54
Range	38.31-44.35	42.68-47.25	37.84-48.78	35.09-52.19	41.65-47.57

fraction may be attributed to the ease of complexation and peptisation products formed between the metal and natural OM like humic and fulvic acid while the low content of Mn in the residual fraction was probably due to low association or retention ability of the mineral's crystal structure, such as with detrital silicates and resistant sulphides (Ogunfowokan *et al*. 2009).

Mobility factor

The value of mobility factor (MF) for five trace metals studied (**Table 10**), with an overall mean for Mn (41.70 ± 2.45); Pb (44.67 ± 1.57); Cd (43.88 ± 3.21); Fe (42.88 ± 1.54); and Zn (44.28 ± 1.54). The value for mobility factor (MF) for Mn decreased in the following order: Hospital (44.35) > Express (44.16) > Bowen (44.08) > Water works (42.49) > Odo-ori (42.48) > Agbowo (41.72) > Adeeke (39.30) > Osogbo (38.41) > Ejigbo (38.31). MF value for Pb decreased in the following order: Water works (47.25) > Ejigbo (46.07) > Osogbo (45.74) > Agbowo (44.83) > Bowen (43.62) > Express (43.48) > Odo-Ori (43.33) > Adeeke (43.21) > Hospital (42.68). MF value for Cd decreased in the following order: Ejigbo >Agbowo > Odo-Ori = Osogbo > Bowen = Express > Adeeke > Water works = Hospital. MF value for Fe decreased in the following order: Water works (52.19) > Bowen (45.09) > hospital (44.73) > Ejigbo (44.63) > Agbowo (42.84) > Adeeke (41.40) > Express (40.32) > Osogbo (39.63) > Odo-Ori (35.09); and MF value for Zn decreased in the following order: Water works (47.57) > Agbowo (44.71) > express (44.49) > Ejigbo (44.38) > Osogbo (44.23) > Hospital (44.07) > Bowen (43.72) > Adeeke (43.45) > Odo-Ori (41.65). A high MF value is an indication of liability and biological availability of heavy metals (Salbu *et al*. 1998) and showed the extent of the vulnerability of living things generally to heavy metals (Ogunfowokan *et al*. 2009). Evidently, the inhabitant of the hospital road in this study have the highest vulnerability to Mn exposure; the inhabitant of water works have the highest vulnerability to Pb exposure; the Ejigbo environment have the highest vulnerability to Cd; and water works environment have the highest vulnerability to Fe and Zn.

Geoaccummulation index

The values for the geoaccumulation index (I-geo) determination for the roadside soils are shown in **Table 11**. Using the total metal levels in the roadside soil with the background levels of heavy metal in non-polluted soils (Turekian and Wadepohl 1961), the roadside soil pollution intensity with respect to the trace metals determined was assessed using the Taylor and McLennan 1995) equation:

$$I\text{-geo} = \log_2 [C_n/1.5B_n]$$

where Cn is the measured total metal concentration in soil; B_n is the background value; and 1.5 is the background matrix correction factor due to lithogenic effects. The I-geo values are classified into seven classes (0-6) as described in **Table 12**.

Table 11 Geo-accumulation Index.

	Mn	Pb	Cd	Fe	Zn
Adeeke	-1.31	-4.09	2.86	-4.89	0.91
Agbowo	-1.48	-3.92	3.03	-4.96	0.82
Bowen	-1.65	-3.89	2.93	-5.16	0.78
Ejigbo	-0.47	-3.89	2.89	-5.13	0.77
Express	-1.73	-3.80	3.09	-5.08	0.76
Hospital	-1.52	-4.08	2.78	-5.01	0.82
Odo-Ori	-1.61	-3.86	3.13	-5.08	0.64
Osogbo	-1.34	-3.83	3.07	-4.96	0.82
Waterworks	-1.53	-3.91	2.93	-5.15	0.72

Table 12 Classification of I-geo values.

Value	Class	Grade/Pollution Intensity
I-geo ≤ 0	0	Practically unpolluted (PU)
0 < I-geo < 1	1	Unpolluted (U) - moderately polluted (MP)
1 < I-geo < 2	2	Moderately polluted (MP)
2 < I-geo < 3	3	Moderately polluted (MP) - heavily polluted
3 < I-geo < 4	4	Heavily polluted (HP)
4 < I-geo < 5	5	Heavily polluted - very heavily polluted
5 < I-geo	6	Very heavily polluted (VHP)

The results of the calculated I-geo values for the street dusts of the study area showed that the street dusts were practically unpolluted with respect to Mn, Fe and Pb; moderately polluted at Adeeke, Bowen, Ejigbo, Hospital and Water Works while Agbowo, Express, Odo-Ori and Osogbo are moderately polluted/Heavily polluted with respect to Cd; all locations were unpolluted/moderately polluted with respect to Zn. This finding showed that there was high level of Cd in the roadside soil of Iwo land.

Correlation analysis

The result of the two-tailed Pearson correlation matrix of the trace metals analyzed are shown in **Table 13**. This result showed that OM was positively correlated with $CaCO_3$ at 0.01 level while both OM and $CaCO_3$ were negatively correlated with Mn and Fe at 0.05 level; Mn was positively correlated with Fe and Zn at 0.01 and 0.05 levels respectively; Pb was positively correlated with Cd at 0.01 level; and Fe was positively correlated with Zn at 0.05 level.

The above associations can be explained in terms of a common source or by chemical similarity (Knudso *et al.* 1977). Therefore, the positive correlation found between OM and $CaCO_3$ could indicate a common source. The inter-element positive correlation between all metals could possibly suggest that the elemental association is controlled by factors such as soil genesis, properties and anthropogenic inputs.

The dependence of trace metal concentrations on traffic density was evaluated by calculation of the Spearman rank correlation coefficient in **Table 14**, which is the adequate test for nonparametric data. The correlations were found to be generally weak and insignificant. This implies that the source of the metals were not actually due to traffic perhaps

Table 13 Two-tailed Pearson's correlation analysis.

	OM	$CaCO_3$	pH	Conductivity	Mn	Pb	Cd	Fe	Zn
OM	1								
$CaCO_3$	0.863**	1							
pH	-0.188	-0.413	1						
Conductivity	0.107	0.047	0.392	1					
Mn	-0.673*	-0.776*	0.103	0.152	1				
Pb	0.385	0.470	0.136	0.363	-0.487	1			
Cd	0.134	0.087	0.389	0.276	-0.251	0.813**	1		
Fe	-0.676*	-0.698*	-0.055	-0.191	0.817**	-0.489	-0.068	1	
Zn	-0.326	-0.273	-0.534	-0.343	0.676*	-0.621	-0.539	0.732*	1

** Correlation is significant at the 0.01 levels

*Correlation is significant at the 0.05 levels

Table 14 Correlation of traffic volume with trace metal concentrations.

	Mn	Pb	Cd	Fe	Zn	Traffic volume
Mn	1					
Pb	-0.603	1				
Cd	-0.410	0.794*	1			
Fe	0.800**	-0.301	-0.059	1		
Zn	0.733*	-0.644	-0.561	0.667*	1	
Traffic volume	-0.083	-0.033	0.077	0.00	-0.133	1

**Correlation is significant at 0.01 level (2-tailed) *Correlation is significant at 0.05 level (2-tailed)

other sources of trace metal contribute significant fractions to the soil burden.

CONCLUSIONS

The levels and chemical speciation studies for five trace metals of roadside soil in Iwo was examined. The analytical results indicate that the levels of trace metals studied were below the literature levels of a typical soil. The undertaken speciation study of five trace metals in the roadside soils revealed differences between these elements in the preferential formation of chemical combinations. There are indications that the Mn and Fe detected were mainly associated with the Mn-Oxide followed by OM fractions in the roadside soils. Zn was associated with OM followed by exchangeable fractions while both Pb and Cd exhibit similar pattern for all the fractions. The physico-chemical analysis revealed that the soils were alkaline. The distribution of the studied metals in the various fractions and results of mobility factor confirm their differences in mobility and bioavailability. Geo-chemical Index study revealed that the soils were practically unpolluted for all the metals studied with exception of Cd which was moderately polluted. The interelement positive correlation between these metals could possibly suggest that the elemental association is controlled by factors such as soil genesis, properties and mainly anthropogenic inputs such as vehicular emissions, lubricating oil, tyre wears and brake lining. Further work on speciation studies of suburb cities with higher traffic volume based on seasonal variations is recommended for future investigations.

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