

Determination of the Chemical Speciation of Trace Metals in Dust Samples and Its Bio-Availability in Kaduna Metropolis.

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Abstract

Trace metals are normally produced from human activities either through the discharge of agricultural, mining, industrial, municipal or residential wastes, automobile, industrial machines and industrial activities. This study was carried out to determine the physico-chemical speciation of trace metals in dust samples and its bio-availability in Kaduna metropolis using sequential extraction techniques. Five geochemical forms (F1-F5) of metals that follows a decreasing solubility and increasing strength of extractant was used. The trace metal concentration was analyzed using Atomic Absorption Spectrophotometer (AAS). Descriptive statistics for the trace metal concentrations of dust samples from different locations within Kaduna metropolis was carried out and result compared with the stipulated guideline limits for metals (in time weighted averages, TWA) in urban dust set by the occupational safety and Health Association (OSHA). Iron had the highest concentration followed by Zinc, Manganese, Cadmium, Lead, Cobalt, Copper and Nickel (Fe > Zn > Mn > Cd > Pd > Co > Cu > Ni). Five successive selective chemical fractions were used in the analysis to determine metals easily exchangeable, associated with Fe-Mn oxide, associated with organic matter, carbonate form and residual fraction. It was found out that the value of Pb, Mn, Zn, Ni Cd and Fe were higher and available in all the sites in the reducible and organic fraction. The exchangeable fraction showed availability of Pb, Mn, Zn, Cd, Ni and Fe at higher values though not at all sites but less than reducible and organic fraction. Carbonate fraction recorded the least values of Pb, Mn, Zn, Cd, Ni and Fe. Co was not available at all in all the fractions while Cu was only available in the organic and residual fraction. Zn, Cd, Mn and Pb, were bio-available while Ni, Cu and Fe were non-available. Due to the bio-availability of these trace metals in the dust, exposure time should be reduced as continuous inhalation and consumption may be injurious to health and can result in death.

Keywords: AAS, Bioavailability, Geochemical, Non-bioavailability, Speciation and Trace metals.

Introduction: Trace metals are elements such as chromium, cobalt, copper, iron, magnesium, selenium, and zinc that normally occur at very low levels in the environment. Living things need very small amounts of some trace metals, as high levels of these metals can be toxic. Iron is an essential element for many living things. In human blood, iron transports oxygen around the body. If too much iron is consumed, however, there can be negative effects on human health (Kelly, Schindler, Hodson, Short, Radmanovich and Nielsen, 2010). Trace metals occur naturally in rocks and soils, but are introduced anthropogenically at higher quantities as micro-pollutants into our environment from several sources such as industrials, agricultural and domestic wastewater/ effluents (Patanaiik, 2010). Aremu *et al.*, (2010) observed that trace metals are introduced into the environment as a result of rock and soil weathering. Environmental pollution is the addition of any substance or form of energy to the environment at

a rate faster than that which the environment can accommodate it. This can be by absorbing, dispersing or breaking it down, causes harm to humans, flora and fauna or abiotic systems. Industrial pollution has been and continues to be a major cause of environmental degradation. Numerous studies have already demonstrated that areas in close proximity to industrial activities are marked by noticeably contamination of air, soil and water (Patanaiik, 2010). Environmental pollution may either be from point source, non point source (diffuse) pollution, and natural or anthropogenic source pollution. Speciation is the determination of concentration of different physicochemical forms of the element, which together make up its total concentration in the sample or the oxidation state/ electronic state, isotopic composition of each species present in a chemical sample (Benson, Winifred and Ifedolapo, 2013).

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Elemental quantification in soils can be achieved through single reagent leaching, ion exchange resins, and sequential extraction procedures. The theory involved in the latter is that the most mobile metals are leached in the first fraction and continue in order of decreasing of mobility. Common examples of the sequential extraction techniques are the Tessier Procedure (Galan, Gómez Ariza, González, Fernández, Morales and Girálde, 2009), the Community Bureau of Reference (BCR) Procedure, the Maiz Short Extraction Procedure, the Galán Procedure, and the Geological Society of Canada Procedure (Amanda and David, 2010). These sequential extraction procedures promote fractionation. This study aims at determining the physico-chemical speciation of trace metals in dust samples and its bio-availability in Kaduna metropolis as metals are not biodegradable and its bio-availability makes the trace metals readily available for plant uptake from the soil and when the plants are consumed by man or animals, they gradually accumulate in the body system resulting in diseases and damage to some organs which may eventually result in death.

Method: Sample Collection and Preparation: Dust samples were randomly collected from different sites in Kaduna metropolis during the dry season for four months from leaves surfaces. The collected leaves were put in a well labelled polythene bag and transported to the laboratory. In the laboratory, the leaves surfaces were washed with distilled water and evaporated to dryness on a hot plate at a temperature of about 70°C in order to obtain the dust. The dust was sieved using 2µm sieve and stored in a well labelled polythene bottle until needed.

Determination of Dust Ph: Exactly 1.0g of dried dust samples were mixed with 20ml of deionized water in a 50ml beaker and stirred with a glass rod. The pH was measured by introducing a glass probe of the pH meter into the dust solution and the reading recorded.

Total Metal Analysis: Exactly 1.0g of the dust sample was weighed into a 100ml beaker (pyrex), and digested with a mixture of 3ml concentrated HNO₃ and 2ml of HClO₄ for 1hour at 100°C in a fume cupboard. After cooling, the mixture was filtered and made up to 50ml volume with distilled water. The digested dust sample was analysed using Atomic Absorption Spectrophotometer (AA-6800) and the results reported in parts per million (ppm). Duplicate determinations were made.

Metals Speciation: Sequential extraction procedure (SEP) based on (Amanda and David, 2010) adopted from (Tessier, Campbell and Bisson, 1979) which defined the five geochemical forms of metals through a careful choice of extractants was used.

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Soluble And Exchangeable Fraction (F1): Exactly 1.0g of the dried dust sample was weighed and extracted with 20ml of a 1M MgCl₂ solution and adjusted to the pH of 7.0 and mechanically shaken for 1hour at 20°C in a polyethylene bottle. Then filtered into a 50ml volumetric flask and made up to 50ml with distilled water. It was analysed using Atomic Absorption Spectrophotometer (AA-6800) and the results reported in parts per million (ppm). Duplicate determinations were made.

Bound To Carbonates (F2): The residue in F1 was extracted with 20ml of a 1M CH₃COONa solution and adjusted to a pH of 5.0 with CH₃COOH by mechanical shaking for 4 hours at room temperature in a polyethylene bottle. The mixture was filtered and the filtrate made up to 50ml volume with deionized water. This was then analysed with Atomic Absorption Spectrophotometer (AA-6800) and the results reported in parts per million (ppm). Duplicate determinations were made.

Bound To Iron And Manganese Oxides (F3): Metals bound to iron and manganese oxides were extracted by pouring 50ml of a 0.04M NH₂OH.HCl and 10ml of 25% CH₃COOH into the residue from F2 in a polyethene bottle and then heated for 6 hours at 96°C in a water bath. The mixture was filtered and the filtrate made up to 50ml volumetric flask with deionized water. This was then analysed with Atomic Absorption Spectrophotometer (AA-6800) and the results reported in parts per million (ppm). Duplicate determinations were made.

Bound To Organic Matter (F4) : Metals bound to organic matter were extracted by pouring 15ml of a 0.02M HNO₃ and 25ml of a 30% H₂O₂ onto the residue from F3. The pH was adjusted to 2.0 with CH₃COOH and then heated for 5 hours at 85°C in a water bath. After cooling, 25ml mixture of 3.2M NH₄OAc and 20% HNO₃ in the ratio of 3:4 was added, followed by continuous shaking for 30 minutes at room temperature. The mixture was filtered and the filtrate made up to 50ml volumetric flask with deionized water. This was then analysed with Atomic Absorption Spectrophotometer (AA-6800) and the results reported in parts per million (ppm). Duplicate determinations were made.

Bound To The Soil Matric Or Residual Fraction (F5): The residue from F4 was quantitatively transferred into 250ml beaker followed by the addition of 10 ml mixture of analytical grade acids HNO₃: HClO₄ in the ratio 5:1. The digestion was performed at a temperature of about 190°C for 1.5 h in a fume cupboard. After cooling, it was filtered and the solution was made up to a final volume (50ml) with deionized water in a volumetric flask. Atomic Absorption Spectrophotometer (AA-6800)

determined the metal concentrations. Duplicate determinations were made.

Statistical Analysis: The results were analyzed statistically using Microsoft Office Excel and the Statistical Package for Social Science (SPSS 23.0 for Windows, SPSS Inc., IL, USA). One-way analysis of variance (ANOVA) followed by Tukey-Kramer's Multiple Comparison was used to assess the variation in concentration of trace metals in the dust samples studied. Results were expressed as mean \pm standard deviation and possibilities less than ($p < 0.05$) were considered to be statistically significant.

Result And Discussion: Total Metal Concentration in Dust Samples: Descriptive statistics for the trace metal concentrations of dust samples from different locations within Kaduna metropolis are given in Table 1 with the stipulated guideline limits for metals (in time weighted averages, TWA) in urban dust set by the occupational safety and Health Association (OSHA). Iron had the highest concentration followed by Zinc, Manganese, Cadmium, Lead, Cobalt, Copper and Nickel. ie Fe > Zn > Mn > Cd > Pb > Co > Cu > Ni. The exceptional high concentration of Fe in the sample could be attributed to the particular type of waste discharged by the industries. Site 2 (Kasupda) which had the highest concentration of Fe is located near a motor garage by the road side and close to a vulchanizer workshop. The activities in the motor garage and repairs by the vulchanizer has also contributed to the high Fe content in this site. The control site recorded the lowest concentration of 609.77 \pm while the highest concentration was recorded in Kasupda Similar work carried out on dust in Accra, Ghana reported high concentration of Fe which ranged from 19782.00-36630.34mg/kg (Atiemo, Ofose, Kuranchie-Mensah and Tutu, 2011, Omaka et al., 2013). These values were higher than the values reported from Fe in this study. The value of 6.54ppm was reported in literature for Fe in dust samples carried out in Ebonyi state (Omaka et al., 2013). This value was for lower than the value of Fe reported in this work. The range of 609.77-11333.80mg/l obtained for this study was considerably higher than 2.18ppm (TWA) Stipulated by OSHA for Fe in air dust (OSHA, 2007).

The value of Zn ranged from 10.74 – 20.81mg/ kg. The highest Zn concentration value was recorded in Kasupda and this value was high when compared to other work reported on Zinc (Atiemo et al., 2011). However, the mean of 14.79mg/ kg reported in this study was significantly higher than the value of 0.752ppm stipulated by OSHA for Zn in air dust (OSHA, 2007). This high concentration may be related to atmospheric deposition and industrial waste discharge. Zinc concentration may also be derived from the mechanical abrasion of vehicles and from zinc compounds used extensively as antioxidants (e.g Zinc carboxylate complexes and sulphates) as detergents dispersant improves for lubricating oils what also agreed with the report of Monika et al. (2011). Concentration of Mn in dust sample ranged

from 3.74-11.55mg/kg with the highest value recorded in secretariat followed by Kasupda which is prone to high traffic congestion while the lowest concentration was recorded in the control. The mean value of 7.40mg/kg of Mn recorded in the study was however, higher than the value of 0.089ppm (TWA) Set as permissible limit for Mn in air (OSHA, 2007). Mufiya et al., (2014) reported the value of 0.002-0.058mg/kg for Mn. Mn is an essential element but very high concentration of it in respirable dust can be dangerous to human health. The high concentration value of Mn may be attributed to anthropogenic activities such as coal fires and tyre wear. Concentration of Cd in the various sites ranged from 0.81-2.12 mg/kg with the highest concentration value recorded in Kasupda, a site prone to very high traffic congestion followed by sites located at commercial areas. Omaka et al., (2003) recorded a lower value of 0.001mg/kg in dust sample for Cd compared to the mean value of 1.80mg/ l recorded in this study. This could be due to the presence of Cd in automobile fuel and soil tends to increase the risk of its intoxication with resultant health effect such as Kidney failure (Saud and Mustafa, 2012). The concentration of Pb in the dust samples range from 0.35 - 3.75mg/kg with the highest concentration value recorded in Kasupda. The mean concentration of 1.77mg/kg for Pb in this study was however lower compared to the range of 33.64-117.45mg/ kg recorded in literature (Atiemo et al., 2011). This concentration value was however higher than the value of 0.006ppm stipulated by OSHA for Pb in air/ dust (OSHA, 2007). This could pose potential threats to humans and environmental media such as water bodies. The high concentration of Pb in this study may be associated with manufacturing of automobile batteries, pigments and cable sheathing. It may also be associated with usage of Pb in plumbing, solders, paints, ceramic ware and plastics.

The value of Cobalt in the study ranged from 0.09-2.69 mg/kg. The highest concentration value of 2.67 mg/kg was recorded in Kasupda followed by NBL, S/R and Secretariat. The lowest concentration of Co was recorded in the control. Similar work carried out reported the range of 11.16-1544.24ppm with a mean value of 506.02ppm for cobalt (Sana`a 2013). This concentration value is very high compared to the mean value of 2.67mg/kg reported in this study. The concentration of Cu determined in the different sites ranged from 0.33-3.03mg/kg with Kasupda recording the highest concentration of Cu. Site 3 and Site1 also recorded slight high concentration of Cu. Although Cu is an essential substance to human life, but in high doses, it causes anemia, liver and kidney damage, stomach and intestinal irritation. The concentration value of Cu reported in this work was higher than the range of 0.025-0.571 mg/kg reported in literature (Mafuyai et al., 2014). This high concentration could be attributed in particulates that originate from weathering of a unique from of a local geological material due to wind erosion, construction work, traffic and residential related activities.

The concentration of Ni ranged from 0.34-0.66mg/kg with a mean value of 0.48mg/kg. Site 2 recorded the highest concentration followed by Secret ariat. These sites are prone

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to high traffic congestion. The high concentration of Nickel may be attributed to anthropogenic activities that emit Ni into the air such as combustion of fuel and residual oil, mining, municipal waste incineration and the high rate of old vehicles plying the road. The mean value of 0.48mg/kg reported in this work was however higher than the range of 0.021-0.216mg/kg reported in literature (Mafuyai, Ishaq, and Rufus, 2014) and lower than the value of 124.52mg/kg reported in Accra (Atiemo et al 2011). In this study Fe recorded the highest concentration followed by Zn. This imply that particulates originated from weathering of a unique form of local geological materials due to wind erosion, construction work, traffic and residential related activities. Zn is one of the commonest element in the earth's crust and if found in air, water, soil and is also present in feeds. It attached to dust particles in the air and rain removes Zn dust particles from air into the soil and water.

Metal Speciation in Dust Samples: The result of speciation studies conducted on the dust samples obtained from the industrial, commercial and the control site is presented in Table 2. The study of distribution of metals, in the different fractions in the samples showed that Mn distributes throughout all the fractions but more pronounced in exchangeable, reducible and residual. It is also observed that the concentration of control samples is lower than the concentration of samples. This indicates that most of Mn in this study has natural sources (Amel, Mohammed, Abdul, Moh and Pauzi, 2012). The percentage of Pb, Zn, Cd, Mn, Cu, Pb, Fe in the exchangeable fraction from all the sites varies from 0.02-33.63% with Mn having the highest and the least was reported for Fe. The high percentage of Fe was recorded in F3 and F5 (Table 2) with the range of 2.36 – 4.95% for F3 and 0.02-22.42% for F5. This indicates that Fe is non- bioavailable. The percentage Fe in the control site is also high which means that major faction of this element in the samples understudy came from natural source. The residual fraction, F5 represent metals largely embedded in the crystal lattice of the soil fraction and should not be available for remobilization except under very harsh conditions (Yusuf, 2007).

The carbonate fraction is influenced by pH, and the observed pH of the dust samples ranged from 5.70 – 7.34. Pb, Zn, Mn, Cd, Ni, Cu and Fe for the study area contribute only about 0.07 – 27.25% in the carbonate fraction. The metals (Pb, Zn, Cd, Ni, Cu) distribute more as reducible, organic and as residual. The higher percentage of metals were from reducible, organic and exchangeable fraction except for Fe which had its higher percentage in the residual fraction (Table2). Metals in the reducible phase are bound to oxides of Fe and Mn in soil. It is well established that Fe exist as nodules, concretions or cement between particles, or simply as coating on particles. These oxides are excellent scavengers for trace metals and are thermodynamically unstable under anoxic conditions (presence of oxygen), hence, changes of anoxic conditions of the soil will either influence the release or retention of elements in the reducible phase (Tessier *et al.*, 1979). The relative percentage abundances exhibited by metals in the oxidizable phase

(organic-bound phase) could be attributed to the organic matter load of soil. On the other hand, it may be due partly to the variations from different agricultural practices and application of agrochemicals on the farmlands around the sampling locations. The anthropogenic inputs differ from one location to the other. Metals concentrations in association with carbonate (oxidizable) fraction are the least in all cases studied. The concentration of metals in this fraction is in agreement with the work reported by Abdus-Salam, Ibrahim and Fatoyinbo (2011) which showed only relatively lower amount of Cd, Pb and Zn in the carbonate fraction. The percentage abundance of Pb is higher in the reducible fraction with the range of 0.71 – 45.71% followed by carbonate and exchangeable fraction in the range of 8.57 – 17.14% and 2.86 – 13.56% (Table 2) with the highest value recorded in the control site. This gives an indication that this element have anthropogenic source. Amel et al (2012) also reported higher percentage concentration of Pb in the predominance of Pb in the reducible fraction is in broad agreement with the fractionation of Pb in street dust (Amel *et al.*, 2012, Ahmed *et al.*, 2012, and Monika and Romic, 2011). Ni showed higher percentage abundance in the organic fraction with the range of 31.82 – 44.12% (Table 2). However, there are also high percentage abundance of Ni in the reducible and the residual fraction in the range of 2.94 – 20.45% and 15.44 – 28.33% respectively.

In the organic fraction, the control site recorded 44.12% which was higher than the percentage abundance recorded in the samples. Reducible and residual fractions recorded higher percentage abundance in all the sites. The chemical association of Cu in the dust is dominated by the residual fraction with the range of 3.63 – 21.25% across the study site. This is in agreement with the findings in Amel et al (2012) who recorded 41% of Cu dominated in street dust. Only about 19.14% is recorded for Cu in the organic fraction in this study. In F1, F2, and F3, Cu was not available. The range of 19.35 – 20.41% was also reported for Cu (Gungshik, Lohdip, and Gongden, 2010). Higher percentage of Zn distributes throughout all the fractions but more pronounced in the reducible. The highest percentage recorded in NBL. Similar studies reported 29.7% Zn in the reducible fraction, 20.9% in the organic fraction and 16.2% in the residual fraction. Earlier studies on dust indicated that larger fractions of Zn were associated with the reducible fraction (Ahmed et al, 2012, Monika et al, 2000). They suggested that Fe and Mn oxides may occlude Zn in the lattice structures. The results for atmospheric particulate dust are similar with high association with Fe-Mn oxides and a lower percentage with the residual fraction (Okunola, Uzairu, Uba, Ezeanyanaso, and Alhassan, 2015). The higher percentage of Cd is observed in the organic fraction with the range of 13.68 – 34.75% followed by carbonate fraction with the range of 10.83 – 15.60%, residual and exchangeable. Cadmium is associated with motor traffic emissions as a constituent of motor alloys or with electronic components and batteries of cars (Chen, Goldberg, Villeneuve, 2008; Okunola *et al.*, 2015).

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Percentage Level Of Bioavailability And Non-Bioavailability:

The comparative bioavailability levels of metals in each site are presented in Table 4. The fate of a metal in an environment is determined by the ease of availability, the higher the level of bioavailability, the higher the impact on the target system. The ease of extraction is related to the degree of solubility and bioavailability of metal form. Therefore, the metal bioavailability factor (MBF) is $F1+F2+F3 / F1+F2+F3+F4+F5$ (Adekola *et al.*, 2010). The operational fractions whose conditions are not easily attainable in the geochemical conditions of the soil are regarded as non-bioavailable fractions (NBF). The value of MBF for elements provides information about their potential mobility in soils and availability to plants (Yusuf, 2007). The value of MBF up to 10% for any element indicates that this element is immobile and unavailable for plants (Torri and Lavado, 2008). In addition to that, the value of MBF up to 50% or greater than 50 % for a particular element suggests that this element is highly mobile and available for plants (Oluwatson, Adeyolanu, Dauda and Akinbola, 2008). The relative abundance of the metals in the mobile fractions of the samples are in the following sequence: Mn>Pb>Zn>Cd>Ni>Fe>Cu (Table 4). The percentage bioavailability of Zn, Cd, Mn and Pb (Table 4) were higher than 50% in all the sites. This indicates that the elements are mobile and are available to plants. The percentage bioavailability and non-bioavailability of Co in all the sites was not available. Zn, Pb and Cd contribute a greater percentage of bioavailable form suggesting that Cd and Pb are highly mobile and are known to accumulate poison in mammals when its concentration is above the threshold (Tokaliolu, Karlal and Birol, 2003). Ni, Fe, and Cu in this study are immobile and unavailable for plants.

Conclusion : Conclusively, the presence of trace metals in the environment is a common phenomenon, especially in areas of high industrial, agricultural and commercial activities due to their non-biodegradable nature. The trace elements can accumulate in ecosystem and food chains, there by resulting in either severe or chronic diseases. The concentration of the metals analyzed were higher when compared with the stipulated guideline limits for metals (in time weighted averages, TWA) in urban dust, set by the occupational safety and Health Association (OSHA). Due to the bio-availability of these trace metals in the dust, exposure time should be reduced as high doses can have toxic and carcinogenic effect resulting in neurologic and hematological complications, nausea, vomiting, and loss of appetite, stomach pains, headaches, diarrhea, hypertension, kidney and liver function disorders.

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Table 1: Total metal concentration in dust samples

	Average Concentration of Metals in Dust Sample					OSHA 2007 (PPM)
	NBL	Kasupda	Stadium	Secretariat	Millenium	
Pb	2.15±0.04 ^b	3.75±0.07 ^a	1.4±0.02 ^c	1.18±0.02 ^d	0.35±0.03 ^c	0.06
Cu	0.93±0.02 ^b	3.03±0.03 ^a	0.96±0.03 ^b	0.8±0.01 ^c	0.33±0.04 ^d	Nil
Zn	14.72±0.1 ^{bc}	20.81±2.18 ^a	15.67±1.9 ^b	12.01±0.59 ^{cd}	10.74±0.39 ^d	0.75
Cd	1.66±0.1 ^b	2.12±0.24 ^a	1.9±0.08 ^{ab}	1.9±0.15 ^{ab}	1.41±0.04 ^b	0.002
Co	1.78±0.12 ^b	2.67±0.68 ^a	1.66±0.05 ^b	0.27±0.05 ^c	0.09±0.02 ^c	Nil
Fe	884.7±85.44 ^b	1133.8±35.40 ^a	805.09±11.38 ^c	1107.22±18.42 ^a	609.77±2.83 ^d	2.18
Mn	6.46±0.33 ^c	8.55±0.71 ^b	6.72±0.09 ^c	11.55±0.47 ^a	3.74±0.19 ^d	0.089
Ni	0.44±0.02 ^b	0.66±0.01 ^a	0.40±0.04 ^b	0.60±0.07 ^a	0.34±0.06 ^b	0.02

NBL =Nigerian Bottling Company, S/R = Stadium Roundabout, SEC = Secretariat, KAP= Kasupda, MILL = Millennium City

Table 2: Metal speciation in dust samples

Fraction	Sample Site	Average concentration of metals (mg/kg)							
		Pb	Cu	Zn	Cd	CO	Fe	Mn	Ni
Exchangeable	NBL	ND	ND	0.42	0.2	ND	0.32	1.5	ND
	KAP	0.16	ND	1.4	0.19	ND	3.17	2.63	0.02
	S/R	0.15	ND	0.28	0.22	ND	0.64	1.39	0.02
	SEC.	0.16	ND	0.47	0.12	ND	0.17	1.36	ND
	MILL	0.01	ND	0.01	0.17	ND	0.13	0.52	ND

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Carbonate	NBL	0.26	ND	0.01	0.21	ND	0.43	0.15	ND
	KAP	0.34	ND	4.63	0.23	ND	6.93	0.32	0.02
	S/R	0.24	ND	4.27	0.25	ND	2.07	1	0.02
	SEC	ND	ND	1.92	0.21	ND	1.01	1.32	ND
	MILL	0.03	ND	2.05	0.22	ND	1.85	0.32	ND
Residual	NBL	ND	ND	6.56	0.19	ND	43.81	1.35	0.09
	KAP	0.52	ND	3.36	0.18	ND	30.06	0.28	0.06
	S/R.	0.01	ND	3.11	0.16	ND	20.98	0.68	0.02
	SEC	0.15	ND	3.07	0.16	ND	26.18	1.53	0.04
	MILL	0.16	ND	2.12	0.17	ND	14.86	0.23	0.01
Organic	NBL	0.29	ND	1.18	0.43	ND	8.2	0.21	0.14
	KAP	0.39	0.58	1.89	0.29	ND	11.35	0.24	0.23
	S/R..	ND	ND	1.74	0.28	ND	7.22	0.23	0.18
	SEC.	ND	ND	1.62	0.31	ND	7.66	0.37	0.23
	MILL	ND	ND	1.17	0.49	ND	3.13	0.13	0.15
Residual	NBL	0.04	0.15	2.5	0.02	ND	198.03	0.93	0.15
	KAP.	0.18	0.11	1.84	ND	ND	194.9	0.59	0.1
	S/R.	0.02	0.05	2.07	ND	ND	138.16	0.69	0.05
	SEC.	0.06	0.17	2.69	ND	ND	248.23	1.18	0.17
	MILL	ND	ND	1.82	ND	ND	111.99	0.56	ND

NBL =Nigerian Bottling Company, S/R = Stadium Roundabout, SEC = Secretariat, KAP= Kasupda, MILL = Millennium City.
 ND =Not Detected

Table 3: Percentage (%) of trace metals in dust samples

Fraction	Sample Site	Pb	Cu	Zn	Cd	CO	Fe	Mn	Ni
Exchangeable	NBL	NA	NA	2.85	12.05	NA	0.04	33.68	NA
	KAP	4.27	NA	6.73	8.96	NA	0.28	30.76	3.00
	S/R	10.71	NA	1.59	11.58	NA	0.08	20.68	5.00
	SEC.	13.56	NA	3.91	6.32	NA	0.02	11.77	NA
	MILL	2.86	NA	0.09	12.06	NA	0.02	13.90	NA
Carbonate	NBL	12.09	NA	0.07	12.65	NA	0.05	2.32	NA
	KAP	9.06	NA	22.25	10.85	NA	0.60	3.74	3.03
	S/R	17.14	NA	27.25	12.16	NA	0.26	14.88	5.00
	SEC	NA	NA	15.98	11.05	NA	0.09	11.43	NA
	MILL	8.57	NA	19.09	15.60	NA	0.30	8.56	NA
Resducible	NBL	NA	NA	45.18	11.45	NA	4.95	20.90	20.45
	KAP.	13.87	NA	16.15	8.94	NA	2.65	3.27	9.09
	S/R.	0.71	NA	19.84	8.42	NA	2.61	10.12	5.00
	SEC	12.71	NA	25.56	8.42	NA	2.36	13.25	6.67
	MILL	13.87	NA	19.74	12.06	NA	2.44	6.15	2.94
Organic	NBL	13.49	NA	12.30	25.90	NA	0.93	3.25	31.82
	KAP	10.40	19.14	9.08	13.68	NA	1.00	2.81	34.85

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	S/R..	NA	NA	11.10	14.74	NA	0.90	3.42	45.00
	SEC.	NA	NA	13.49	16.32	NA	0.69	3.20	38.33
	MILL	NA	NA	10.89	43.75	NA	0.51	3.48	44.12
Residual	NBL	1.86	16.13	16.98	1.20	NA	0.02	14.39	15.44
	KAP.	4.80	3.63	8.84	NA	NA	17.19	6.90	15.15
	S/R.	1.43	5.21	13.21	NA	NA	0.17	10.27	5.40
	SEC.	5.08	21.25	22.39	NA	NA	22.42	10.22	28.33
	MILL	NA	NA	16.95	NA	NA	18.37	14.97	NA

NBL = Nigerian Bottling Company, S/R = Stadium Roundabout, SEC = Secretariat, KAP = Kasupda, MILL = Millennium City, NA = Not Available

KEY: Percentage (%) of trace metals =
$$\frac{\text{Concentration of metal}}{\text{Total metal concentration}} \times 100 \dots (3)$$

Table 4: Percentage level of bioavailable and non-bioavailable fractions

Fraction	Sample site	Pb	Cu	Zn	Cd	Co	Fe	Mn	Ni
	NBL								
Bioavailable		44.1	NA	61.9	57.1	NA	17.8	72.5	23.7
Non-bioavailable		55.9	15	38.1	42.9	NA	82.2	27.5	76.3
	KAP								
Bioavailable		64.2	NA	71.6	67.4	NA	16.3	79.6	23.2
Non-bioavailable		35.9	69	28.4	32.6	NA	83.7	20.4	76.7
	S/R								
Bioavailable		95.2	NA	66.8	69.2	NA	14	76.9	20.7
Non-bioavailable		4.76	5	33.2	30.8	NA	86	23.1	79.3
	SEC								
Bioavailable		83.8	NA	55.9	61.3	NA	9.91	73.1	9.09
Non-bioavailable		4.76	5	33.2	30.8	NA	86	23.1	79.3
	MILL								
Bioavailable		100	NA	58.3	53.3	NA	12.8	60.8	6.25
Non-bioavailable		NA	NA	41.7	46.7	NA	87.2	39	93.8

NBL = Nigerian Bottling Company, S/R = Stadium Roundabout, SEC = Secretariat, KAP = Kasupda, MILL = Millennium City (control), NA=Not Available

KEY:

(%) Bioavailability =
$$\frac{\text{Exchangeable} + \text{Carbonate} + \text{Reducible}}{\text{Exchangeable} + \text{Carbonate} + \text{Reducible} + \text{Organic} + \text{Residual}} \dots (4)$$

(%) Non-bioavailability =
$$\frac{\text{Organic} + \text{Residual}}{\text{Exchangeable} + \text{Carbonate} + \text{Reducible} + \text{Organic} + \text{Residual}} \dots (7)$$

(Adekola, Abdus-Salam, Bale and Oladeji, 2010).

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