Distribution of Metals in Urban Street Dusts of Benin City, Nigeria

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Abstract. Dust samples were collected from 30 sites within Benin city, Nigeria, during the month of December, 2006 - March 2007 and analysed for Cu, Cr, Ni, Cd and Pb using atomic absorption spectrophotometry. The samples were divided into 3 categories, including a control. Results showed that the dust samples contained significant levels of the metals studied compared to the control site. The mean values for Cu, Cr, Ni, Cd and Pb were 16.83 mg/kg, 55.40 mg/kg, 5.91 mg/kg, 3.17 mg/kg, and 182 mg/kg, respectively, for the high traffic density. The mean concentrations of Cu, Cr, Ni, Cd and Pb were 11.98 mg/kg, 52.21 mg/kg, 6.89 mg/kg, 3.92 mg/kg and 167.34 mg/kg, respectively, for the medium traffic areas, while mean concentrations of Cu, Cr, Ni, Cd and Pb in the low traffic areas were 10.46 mg/kg, 58.7 mg/kg, 8.06 mg/kg, 3.49 mg/kg and 142.53 mg/kg, respectively. These values suggest that motor vehicles and electricity generating sets formed the major sources of these metals in the dust samples. The values of metals in the dust samples in these areas were compared with the results of investigations in other countries and these values at various zones of Benin city were found similar, which indicates that Benin city can be considered as one big urban centre with high population and traffic density.

Keywords: heavy metals, contamination, dust, vehicular emission; electricity generating sets

Introduction

Air pollution is a major environmental problem associated with rapid urbanization and industrial growth. Human activities are responsible for the mobilization of metals into the biosphere thereby contributing an important process in the geochemical recycling of these contaminants (Addo et al., 2012). Dust is a complex mixture of particulates with a varied chemical composition resulting from the interact of solid, liquid and gaseous materials produced from different sources, processes and activities (Addo et al., 2012; Hjotenkrans et al., 2006; Singh et al., 2005). Urban dusts have been implicated for its potential to carry high load of myriads of environmental pollutants such as metals, PAHs and PCBs etc. (Faiz et al., 2009; Lu et al., 2009). The occurrence of high concentrations of metals in dust particles are potential hazard to human health especially to children (Yap et al., 2012; Meza-Figueroa et al., 2007) who often play in the street, school yard, parks, etc. The main source of road dust is deposition of atmospheric aerosol particles. In urban environment, these particles originate mainly from road traffic,

emissions from industries, construction activities and from the flaking of paints (Radojevic and Bashkin, 1999). Particles larger than 10 μ m in diameter are deposited quite rapidly to the earth surface under the influence of gravity. The study of metal in dust particles is important because dust can be freely inhaled by those transversing the streets and those residing within the streets. Dust is one of the major mediums through which metals find its way into soil, surface and groundwater after the rain shower (Tamrakar and Shakya, 2011). In many developing countries, where urban pollution levels are especially high, a large number of children live in the roadsides and spend most of the day on the street under conditions of poor hygiene and subsequently ingests this dust.

Occurrence of metals in the environment is of great concern because some of these metals are essential for normal growth, while others can not be tolerated at even low concentrations due to their toxicity. For example, lead toxicity is characterised by symptoms such as anaemia, colic, neuropathy, sterility and coma. Exposure to low doses of lead has been implicated for behavioural abnormalities, learning disabilities, impaired hearing and cognitive function in human (Chauhan *et*

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al., 2010). Lead can freely cross the placenta during pregnancy causing intrauterine foetal death, premature delivery and low birth weight (Papanikolaou et al., 2005). Blood lead level of approximately 10 µg/dL could lead to increased risk of pregnancy hypertension, spontaneous abortion and reduced offspring neurobehavioural development (Bellinger, 2005). Cadmium is known to impair kidney function, reproductive capacity, cause hypertension, tumour, hepatic dysfunction (Iwegbue, 2011) and skeletal damage (Jarup, 2003). The toxicity of Cd is associated with its ability to displace physiologically appropriate metals such as Cu and Fe in cytoplasmic and membrane proteins (Marias and Blackhurst, 2009). Chromium (VI) is a known carcinogen. At higher concentrations, Cr, Cu and Zn are associated with toxicity symptoms such as nephritis, anuria and extensive lesions in the kidney (Iwegbue, 2011).

Street dust has several advantages for pollution monitoring, since the heavy metals are present at concentrations that make it possible to obtain samples and analysis without disturbing the ecosystem, which gives room for large scale and repeated sampling (Ayodele and Gaya, 1998). Though there are numerous studies of heavy metal contamination of urban dusts in developed countries, little information is available on heavy metals of urban dusts of developing countries (Banerjee, 2003) including Nigeria, where relatively few studies on metals contamination of urban dusts have been documented (Shinggu et al., 2007; Mashi et al., 2005; Ayodele and Gaya, 1998). The objective of the present study is to determine the concentrations of five metals (Cu, Cr, Ni, Cd and Pb) in urban street dusts from Benin city with a view of providing information on the sources and risk associated with metal contamination of urban dusts.

Materials and Methods

Description of study area. The study area (Benin city) lies within the latitude 6°.20'N and 6°.31'N and longitude 5°.35'E and 5°.41'E. The mean annual rainfall in this area ranges between 2540-3500 mm. In certain years, the mean annual rainfall could rise to above 4000 mm. The temperature for this area ranges between 28 °C and 33 °C around March and 23 °C and 31 °C in August. The relative humidity of the area is highest in August and ranges between 80-90%. It is lowest between November and March (60-85%). Two rivers (Ogba and Ikpoba) formed the drainage system of Benin city.

The principal industries in Benin city are brewery, pharmaceutical, food processing company and furniture industries. Other mediums scale industrial activities include welding and fabrication, bronze casting etc.

Sampling. Dust samples were collected from 30 sites within Benin city for a monthly period of December 2006 to March 2007. The high traffic zones had traffic density of 10,000 - 12,000 vehicles/day; medium traffic zones have traffic density of 6000 - 8,000 vehicles/day and the low traffic density zones have traffic density less than 5,000 vehicle/day. Samples were collected using a clean plastic dustpan and a brush (Akhter and Madany, 1993). The dust samples were collected at monthly interval for the above period from each site. A control site sample was collected from a rural settlement at the outskirt of the city in Egor Local Government area (the control site has traffic density of less than 50 cars/day). The dust samples were oven dried at 40-60 °C, sieved, and stored in a polyethylene containers at 4 °C prior to analysis.

Reagents. All reagents used were of analytical grade, working standards of cadmium, chromium, copper, nickel and lead were prepared by diluting concentrated stock solution (Merck Darmstadt, Germany) of 1000 mg/L with 0.25 M HNO₃.

Sample Preparation. One gram of the dust samples of each site were placed in a Kjeldahl flask and 15 mL of aqua regia was added and swirled to wet the samples. The samples were allowed to stand overnight. In the next day, the flask was placed in heating block and heated to 50° C for 30 min and raised to 120 °C and continued for 2 h. The digest was cooled to room temperature and dissolved in 10 mL of 0.25 M HNO₃ and filtered through Whatman No. 1 filter paper and made up to 50 mL with 0.25 mol/L HNO₃.

Chemical analysis. All digested samples were analysed in triplicate using graphite flame atomic absorption spectrophotometry (GBC scientific equipment SENS AA, Melbourne, Australia) equipped with D₂ background corrective device.

Quality control and statistical analysis of results.

Quality control was assured by the use of procedural blanks prepared in a similar manner like the samples and spike recovery method (SRM). Reagent blanks were used to correct all instrument readings. All glassware was cleaned with 10% HNO₃ for 48 h then rinsed with deionised water. The spike recoveries for each of the elements screened were greater than 93%.

Results are expressed as mean± standard deviation SD and one way analysis of variance was carried out using a statistical analysis system (SPSS version 12). Differences in the concentrations of the elements within a given zone were tested with ANOVA. Turkey multiple-comparison test was used to compare the differences in the mean values of the elements from different zones and principal component analysis was used to establish relationship between the metals.

Contamination assessment methods of the street dust. There are several ways of expressing the contamination levels of soil and sediments. The most common ways include index of geoaccumulation and enrichment factor (Addo *et al.*, 2012). In this study, geoaccumulation (Igeo), enrichment factor (EF), contamination factor (CF) and pollution load index (PLI) have been applied to assess the metal contamination levels of urban street dust of Benin city.

Index of geoaccumulation (Igeo). The index of geoaccumulation (Igeo) was originally used to assess the extent of metal contamination of sediment (Muller, 1969) which has been applied here.

The index of geoaccumulation is given by the formula

$$I_{geo} = log_2 \left[\frac{C_n}{1.5 B_n} \right]$$

where:

Cn = measured concentration of the metal in the tested sample (street dust)

B_n = the geochemical background value of the element in fossil argillaceous sediment (continental crusted average or average shale).

However, the mean value of metals at the control site was used as background concentration in this study.

The constant 1.5 is introduced to minimize the effect of possible variations in background values which may be attributed to lithologic variation in the sediment (Addo *et al.*, 2012; Lu *et al.*, 2009).

The interpretation for the geoaccumulation index is as follows: Igeo < 0 = practically unpolluted; 0 < Igeo < 1 = unpolluted to moderately polluted; 1 < Igeo < 2 = moderately polluted, 2 < Igeo < 3 = moderately to strongly polluted; 3 < Igeo < 4 = strongly polluted; 4 < Igeo < 5 = strongly polluted and Igeo > 5 = extremely polluted to very polluted.

Enrichment factor. Contamination factor (Enrichment factor) and pollution load index. The contamination factor reflects metal enrichment in the dust.

$$CF = C_{metal}/C_{background}$$

where:

CF is the contamination factor, $C_{\rm metal}$ is the concentration of pollutant in the dust; $C_{\rm background}$ is the value of the metals.

In this study, the concentration of metals at the control site was used as the background concentration for the metals, where the contamination factor CF < 1 refers to low contamination, 1 < CF < 3 indicate moderate contamination; 3 < CF < 6 indicates considerable contamination and CF > 6 indicates very high contamination. Enrichment factor can give an insight to differentiating an anthropogenic source from a natural origin as well as assessment of the degree of metal contamination. Five contamination categories are recognised on the basis of enrichment factor (Loska et al., 2003; Sutherland et al., 2000). The contamination categories based on EF values include: EF < 2 deficiency to minimal enrichment; EF = 2-5 moderate enrichment; EF = 5 - 20 significant enrichment; EF = 20 - 40 very high enrichment; EF > 40 extremely high enrichment.

Each site was evaluated for the extent of metal pollution using the pollution load index (PLI) developed by Thomilson *et al.* (1980). The PLI is given by the expression

$$PLI = {}^{n}\sqrt{CF_{1} \times CF_{2} \times CF_{3} \times \times CF_{n}}$$

where:

n is the number of metal studied (five in this study)

The PLI provide simple but comparative means for assessing a site quality, where a value of PLI < 1 denotes perfection, PLI = 1 indicates that only baseline levels of the pollutants are present and PLI > 1 would indicate deterioration of site quality (Thomilson *et al.*, 1980).

Results and Discussion

The overall mean concentrations of Cu, Cr, Ni, Cd and Pb in the dust samples from high, medium and low traffic density zones are presented in Table 1, while Table 2 presents the mean values for each element at each site in the different zones. The values in parenthesis represent concentration range. Analysis of variance on the average of all data of each location over sampling period (December 2006 - March, 2007) showed no significant difference in the concentrations of copper, chromium, nickel, cadmium and lead at 95% probability level except for sites HTD₅ and HTD₉. However, there

HTD		MTD		LTD		
Metals	Range	Mean	Range	Mean	Range	Mean
Cu	0.05-43.0	16.83±12.26	3.20-21.10	11.98±6.51	5.90-15.90	10.46±4.02
Cr	0.05-123.0	55.40±34.30	16.00-92.30	52.21±25.49	6.80-103.80	58.70±36.91
Ni	0.05-38.20	5.91 ± 10.67	0.05-44.20	6.89 ± 15.42	0.05-22.10	8.06 ± 9.99
Cd	0.05-11.50	3.17±3.75	0.05-9.20	3.94 ± 3.85	0.05-7.10	3.49 ± 2.89
Pb	83.70-294.30	182.06±51.44	131.70-195.90	167.34 ± 23.14	104.4-179.30	142.43 ± 29.28

Table 1. Overall mean concentration of metals (mg/kg) in difference traffic density areas

HTD = high traffic density; MTD = medium traffic density; LTD = low traffic density.

are significant variations in the metal concentrations when various sites were compared. All sites showed higher levels of the metals than the control site except for Cd, Cr, and Cu in some sites, which indicates that levels of metals at such sites are not resulting from pollution, rather due to natural background levels.

The mean levels of Cu in the dust samples ranged from 0.05 - 43.0 mg/kg, 3.20 - 21.10 mg/kg and 5.90-15.9 mg/kg for high medium and low traffic density zones, respectively. Significant higher levels of Cu were observed in sites HTD₇ and HTD₃ as compared with any other sites. The high traffic density zone recorded higher levels of Cu as compared with medium and low traffic density zones. Copper in the dust particles are derived from engine wear, from thrust bearing, bushing and bearing metals (Jaradat and Momani, 1999). Other sources of Cu in the studied areas include contamination from furniture manufacturing industries which are situated along the major runways in the city. It has been noted that chemicals such as copper sulphate, boliden salt (BIS salt) mixed with sulphate and chromate copper arsenate (CCA) have been used as preservatives in wood industries (Bhattacharya et al., 2002). The levels of Cu found in this study are consistent with the levels reported for urban dusts (El-Hassan et al., 2006; Dandar and Palar, 2003), however, comparatively lower than some other cities in the world (Table 3).

The mean concentrations of Cr in the dust samples follow the order; low traffic density zone > high traffic density zone > medium traffic density zone. The concentrations of Cr range between 0.05-123 mg/kg, 16-92.30 mg/kg and 6.80-108.8 mg/kg for high, medium and low traffic density zones, respectively. The highest mean levels of Cr were observed at sites HTD₁₄ and MTD₃ and LTD₇ for high, medium and low traffic density zones, respectively. Overall, the mean values of Cr in the three zones are similar. Studies have shown

that stainless steel and alloyed steel contains Fe, Cr, Co, Al and/or Cu and that exhaust emission from both gasoline and diesel vehicles contain variable quantities of the elements (Chong, 1986). However, metal fabrication, woodwork, bronze casting and paint flaking contribute variable amounts of chromium in this city, Table 3 shows the levels of Cd, Cu, Cr, Pb and Ni in this study compared with some other cities.

The concentrations of Ni on the dust samples ranged between 0.05-38.20 mg/kg, 0.05-44.0 mg/kg and 0.05-22.10 mg/kg for high, medium and low traffic density zones, respectively. Elevated level of Ni was observed at sites HTD₁ and HTD₄ for high traffic density zone, while sites LTD₁ and LTD₂ have higher levels of Ni compared to any other sites in the low traffic density zone. However, Ni is a fuel additive as Pb, especially in burning fuel (diesel) that are used for electricity generator in the residential areas (Sheppard et al., 2000). The mean concentrations of Cd in the dust samples ranged between 0.05 - 11.50 mg/kg, 0.05 - 9.20 mg/kg, and 0.05 - 7.10 mg/kg for high, medium and low traffic zones, respectively. In all, 33% of the studied sites had Cd concentrations similar to that of the control sites. The highest level of Cd was observed at site HTD₁₁ (11.50 mg/kg). Metal plating, burning of plastics, pigment, burning of fossil fuel, metallurgical process and tyre rubber are major sources of Cd. Cadmium is also found in lubricating oil as part of many additives. It has been reported that the levels of Cd in car tyres range from 20-90 mg/kg as associated with Cd in the process of vulcanisation (Massadeh and Snook, 2000; Jaradat and Momani, 1999). In the absence of major industries in the sampling sites, the levels of Cd could be due to lubricating oils and/or older tyres, that are frequently used and the rough surfaces of the roads which increase the wearing of tyres. Natural background levels of soil Cd ranged from 0.01 - 0.7 mg/kg, urban

Table 2. Mean concentration $(mg/kg) \pm SD$ ranges of heavy metal in dust

Zones	Samples site ID	Cu	Cr	Ni	Cd	Pb
High traffic	HTD ₁	6.60±0.98	49.66±6.45	44.20±5.30	0.05±0.01	131.70±18.44
	•	(5.61-7.95)	(13.21-56.11)	(38.50-19.50)	(0.04-0.06)	(113.28-150.14)
	HTD_2	9.61 ± 1.63	62.70 ± 9.78	16.80 ± 2.18	0.05 ± 0.02	83.70±13.39
	-	(7.98-1.24)	(52.92-72.48)	(14.62 - 18.98)	(0.04-0.07)	(70.38-97.09)
	HTD_3	0.05 ± 0.01	63.50±11.43	0.05 ± 0.01	0.05 ± 0.01	144.30±17.32
		(0.04-0.06)	(52.07-74.95)	(0.04-0.06)	(0.03-0.06)	(126.98-161.62)
	HTD_4	39.80 ± 1.78	0.05 ± 0.01	38.20 ± 5.73	0.70 ± 0.13	148.90+19.36
		(35.12-11.58)	(0.04-0.06)	(32.47-13.93)	(0.57 - 0.83)	(129.54-168.26)
	HTD_{5}	9.60 ± 1.15	17.80 ± 15.13	8.80 ± 1.14	4.50 ± 0.77	141.60±21.24
		(8.15-1.72)	(102.49-133.11)	(7.66-9.94)	(3.73-5.27)	(120.36-162.84)
	HTD_{6}	16.66±1.15	63.70±8.28	13.10±1.73	8.20±1.07	203.70±36.67
		(12.45-20.75)	(55.42-71.98)	(11.37-14.83)	(7.13-9.27)	(1 67.03-240.37)
	HTD_{7}	21.70±3.47	84.10±10.93	0.05±0.01	0.05±0.01	209.60±3.68
		(18.23-25.17)	(73.17-95.03)	(0.04-0.06)	(0.04-0.06)	(174.22-245.56)
	HTD_{8}	43.00±5.16	48.50±4.85	0.05±0.01	0.05±0.01	209.90±33.58
		(37.84-48.16)	(43.65-53.35)	(0.03-0.07)	(0.04-0.06)	176.32-243.48)
	HTD_9	27.80±5.28	66.30±8.62	0.05±0.01	0.05±0.0 1	209.90±27.29
		(22.53-33.08)	(57.68-74.92)	(0.04-0.08)	(0.03-0.07)	(182.6-237.19)
	HTD_{10}	9.00±2.70	34.60±6.23	0.05±0.01	3.50±0.53	184.60±33.23
	LITTO	(6.30-11.70)	(28.37-40.83)	(0.03-0.06)	(2.97-4.03)	(151.37-217.83)
	HTD_{11}	6.00±0.36	0.05±0.02	0.05±0.02	11.50±1.95	294.30±50.03
	LITE	(5.64-0.36)	(0.01-0.07)	(0.04-0.07)	(9.90-13.46)	(244.27-344.33)
	HTD_{12}	14.60±1.75	64.60±8.40	9.50±10.34	0.05±0.01	184.50±33.20
	LITE	(12.85-16.35)	(73.00-56.20)	(8.15-10.83	(0.03-0.06)	(151.30-217.70)
	HTD_{13}	17.80±1.78	26.70±4.27	0.05±10.02	3.10±0.56	236.70±37.87
	LITE	(16.02-19.58)	(22.43-30.97)	(0.03-0.06)	(2.54-3.66)	(198.83-274.57)
	HTD_{14}	6.70±1.05	123.00±22.14	0.05±0.02	8.70±1.22	212.50±34.00
	LITD	(5.65-7.75)	(100.86-145.14)	(0.04-0.07)	(7.48-9.92)	(178.50-246.50)
	HTD ₁₅	11.60±1.97	40.20±5.63	0.05±0.01	1.90±0.27	170.50±30.69
	LITD	(9.63-13.57)	(4.57-45.83)	(0.04-0.06)	(1.63-2.24)	(139.81-201.19)
	HTD_{16}	21.60±3.24	58.00±8.70	11.25±1.46	5.20±0.88	128.10±21.78
	LITD	(18.36-21.84) 11.50±2.07	(19.30-66.70) 41.80±5.43	(9.79-12.71) 0.05±0.02	(4.32-6.08) 0.05±0.01	(106.32-149.88) 152.60±1 .3 I
	HTD_{17}	(9.43-13.57)	(36.37-47.23)	(0.03 ± 0.02)	(0.03 ± 0.01)	(134.29-170.91)
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Medium	MTD_1	9.80±1.86	29.70±3.86	0.05±0.01	9.20±1.20	160.50±28.89
traffic	MED	(7.94-11.66)	(25.81-33.56)	(0.05-0.06)	(9.00-10.4)	(131.61-189.39)
density	MTD_2	18.40±2.76)	65.30±9.14	0.05±0.01	9.00±1.17	179.60±23.35
	MTD	(15.65-21.16)	(56.16-74.44)	(0.04-0.06)	(7.83-10.17)	(156.25-202.95)
	MTD_3	21.10±1.01	92.30±12.00	1.20±0.19	5.90±1.00	189.00±4.57
	MTD	(17.09-25.11)	(80.30-104.30)	(1.01-1.39)	(4.90-6.90)	(164.43-213.57)
	MTD_4	5.90±0.89 (5.01-6.79)	16.00±1.76 (14.24-17.76)	0.05 ± 0.01 (0.03-0.07)	3.00±0.38 (2.62-3.38)	195.90±27.43 (168.47-223.33)
	MTD_5	3.20±0.32	69,90±8.39	0.05 ± 0.02	4.30±0.60	15 1.00±16.61
	W11D ₅	(2.88-3.52)	(61.51-78.29)	(0.01-0.06)	(3.70-4.63)	(134.39-167.61)
	MTD_6	16.20±2.27	30.30±4.55	0.05 ± 0.02	0.05±0.01	146.50±19.05
	WIID ₆	(13.93-18.17)	(5.75-34.85)	(0.03-0.07)	(0.04-0.06)	(127.45-165.55)
Low traffic	LTD	13.40±2.28	62.10±6.83	20.00±3.00	7.00±1.19	139.10±19.47
density	LTD ₁					
density	LTD ₂	(11.1-15.68) 5.90±0.59	(55.27-68.41) 70.90±11.34	(17.00-23.00) 22.10±3.98	(5.81-8.19) 0.05±0.01	(119.63-158.57) 162.10±19.45
	212	(5.31-6.19)	(59.56-82.24)	(18.12-26.08)	(0.04-0.06)	(142.65-181.55)
	LTD ₃	14.40±1.73	12.20±1.34	0.05 ± 0.01	2.60±0.31	123.40±14.81
	2123	(12.67-16.13	(10.86-13.54)	(0.03-0.06)	(2.29-2.92)	(108.60-138.21)
	LTD_4	8.50±1.36	6.80±0.88	12.80±2.05	3.60±0.47	104.40±15.66
	2124	(7.14-9.86)	(5.92-7.68)	(10.75-14.85)	(3.13-4.07)	(88.74-1 2J.06)
		(,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,		0.05±0.01	4.00±0.60	172.70±24.18
	LTD ₅	15.90±2.39	91.90±13.79	0.05±0.01	4.00±0.00	
	LTD ₅	15.90±2.39 (13.51-19.29)	91.90±13.79 (78.11-105.69)		(3.40-4.60)	
	<u>J</u>	(13.51-19.29)	(78.11-105.69)	(0.04-0.06) 0.05±0.01	(3.40-4.60)	(148.52-196.88)
	LTD ₅	(13.51-19.29) 6.70±0.87	(78.11-105.69) 63.20±7.58	(0.04-0.06) 0.05±0.01	(3.40-4.60) 0.05±0.01	(148.52-196.88) 116.70±17.51
	LTD ₆	(13.51-19.29) 6.70±0.87 (5.83-7.57)	(78.11-105.69)	(0.04-0.06) 0.05 ± 0.01 (0.04-0.06)	(3.40-4.60)	(148.52-196.88)
	<u>J</u>	(13.51-19.29) 6.70±0.87 (5.83-7.57) 8.40±1.18	(78.11-105.69) 63.20±7.58 (55.62-70.78) 108.80±14.4	(0.04-0.06) 0.05±0.01 (0.04-0.06 1.40±0.17	(3.40-4.60) 0.05±0.01 (0.04-0.06) 7.10±1.14	(148.52-196.88) 116.70±17.51 (99.19-134.21) 179.30±23.3!
Control site	LTD ₆	(13.51-19.29) 6.70±0.87 (5.83-7.57)	(78.11-105.69) 63.20±7.58 (55.62-70.78)	(0.04-0.06) 0.05 ± 0.01 (0.04-0.06)	(3.40-4.60) 0.05±0.01 (0.04-0.06)	(148.52-196.88) 116.70±17.51 (99.19-134.21)

Table 3. Distribution of metals	(mg/kg) in dus	t particles in son	ne countries of the world
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Country/City	Pb	Cd	Cu	Ni	Cr	Reference
Benin city (Nigeria)	83.70-294.30	0.05-11.5	0.05-43.0	0.05-44.20	0.04-123.0	This study
Turkey (Adapazari)	25.9	0.7	14.2	40.2	10.25	Dandar & Palar, 2003
Kuwait (Bahrain)	697.2	72.0	-	125	144	Akhter & Madany,1993
United Kingdom	266	4.54	-	-	-	Massadeh & Snook, 2000
Jordan	25.09-75.33	2.36-2.83	14.33	17.36-22	14.1-18	El- Hassan et al., 2006
Australia (Jackson)	487	-	164	27	34	Birch and Scolen, 2003
Nigeria (Mubi)	20.2-35.37	0.59-1.33	11.63	nd-8.62	d-5.40	Shinggu et al., 2007
Poland (Kazowiekie)	576.9	10.8	521.6	40	295	Krolak, 2000
Turkey (Istanbul)	368	0.3	191.1	27.1	-	Yetimoglu et al., 2007
Turkey (Kayseri)	49-381	1.45	12-315	23-85	31-39	Divrkli et al., 2005.
China	230.52	-	94.98	-	167.28	Yomgming et al., 2006
Mexico	32.113	2.112	-	-	-	Benin et al., 1999
Nigeria (Gwagwalada)	210	3.9	97	-	-	Mashi et al., 2005
China (Boaji)	433.2	-	123.2	48.8	126.7	Lu et al., 2010
Ghana (Ketu-South)	22.89	-	60	73.45	744.5	Addo et al., 2012
Nepal (Kathmandu)	12.3 - 116.8	0.3 - 39.6	-	4.9-86.3	1.4 - 14.3	Tamrakar and Shakya, 2011
Bangladesh (Dhaka City)	54	-	105	35	135	Ahmed and Ishiga, 2006

value range from <0.01-8.0 mg/kg, superfund cleanup goal are 2- 20 mg/kg. The levels of Cd observed in the three zones did not exceed the superfund cleanup goal of 20 mg/kg.

In high traffic density zone, higher mean values of Pb were observed at sites HTD₁₁, HTD₁₃, HTD₁₄ with mean concentrations of 294.3 mg/kg, 236.7 mg/kg, 212.5 mg/kg, respectively. In the medium traffic zone, higher mean values of lead were observed at sites MTD₄ 195.9 mg/kg and MTD₃ 189.0 mg/kg, respectively. The high traffic density zone showed overall higher mean level of Pb in comparison with the medium and low traffic density zones. The major sources of lead in the dust samples are due to vehicular emission. Lead tetraethyl has been used as an anti-knock agent in gasoline in Nigeria. The similarity in the concentrations of lead in the various zones indicated that Benin city can be considered as one big urban centre with high population and traffic density. Due to the epileptic power supply in the city, most households and business outfits uses various kinds of electricity generators that uses gasoline which contribute significant amounts of lead to the urban environment. Yetimoglu et al. (2007) reported mean lead concentration of 368.3 mg/kg in street dusts collected from Pandik to Levent in E-5 in Istanbul, Turkey.

Index of geoaccumulation, enrichment factor and pollution lood index. Geoaccumulation index, enrichment factor and the pollution load index of metals at the examined sites are presented in Table 4. The Igeo for Cu at these sites ranged between -7.17 to 2.47 for

high traffic density areas. In the high traffic density zones, only six sites had Igeo value less than 1. The Igeo value of copper in the medium traffic areas ranged from -1.17 to 1.55 and -0.29 to 1.14 for low traffic density areas. In overall, 16 out of 30 sites examined had Igeo values < 1, while 14 sites had Igeo value > 1 < 3, which falls within the moderately strongly polluted range.

Two sites had Igeo values for Cr < 1. The Igeo values for Cr ranged between -6.83 and 4.43. Nineteen sites had Igeo value > 3. Based on the Igeo classification, majority of these sites were strongly polluted with Cr. The Igeo values for Ni ranged from -0.59 – 9.2 with 16 sites having Igeo values < 1 and 12 sites had Igeo values for Ni > 5 (i.e. in the extremely polluted range), while two sites had Igeo values of Ni > 4 < 5. The Igeo values for Cd range between -0.59 and 7.26. Majority of these sites (20 sites) had the Igeo values for Cd > 3, while all other sites had Igeo values < 1. In the case of Pb, all sites in the three zones had Igeo value ranging from 1.43 to 2.93. On the basis of Igeo classification, these sites can be classified as moderately to strongly polluted with Pb.

Enrichment factor (EF) can give an insight to differentiating anthropogenic sources from a natural origin as well as assessing the degree of metal contamination. The concentration factors (CF) values for metals ranged from 1.23-8.96, 0.01-32.37, 1.00-4.42, 1.00-844 and 1.0-174 for Cu, Cr, Ni, Cd and Pb, respectively. According to Zhang and Liu (2002), the EF values between 0.5-1.5 indicates that the metal is entirely from crusted material or natural processes, whereas, EF

Table 4. The index of geoaccumulation (Igeo), concentration factor (CF) and pollution load index (PLI) of metal in urban street dust of Benin city, Nigeria

Site		Cu	Cr	Ni	Cd	Pb	PLI
HTD ₁	Igeo	-0.13	3.12	9.2	-0.59	2.09	
1	CF	1.40	13.1	844.0	1.0	6.38	10.1
HTD_2	Igeo	0.42	3.46	7.81	-0.59	1.43	
_	CF	2.00	16.50	336.0	1.0	4.05	8.52
HTD_3	Igeo	-7.17	3.49	-0.59	-0.59	2.22	
	CF	0.01	16.71	1.0	1.0	6.99	1.03
HTD_4	Igeo	2.47	-6.83	8.99	3.22	2.27	
	CF	8.29	0.01	764.0	14.0	7.21	6.08
HTD_5	Igeo	0.42	1.64	6.88	5.91	2.19	
	CF	2.00	4.68	176.0	90.0	6.86	15.90
HTD_{6}	Igeo	1.21	3.48	7.45	6.77	2.72	
	CF	3.47	16.76	262.0	164.0	9.86	30.1
HTD_7	Igeo	1.59	3.88	-0.59	0.59	2.8	• • •
	CF	4.52	22.13	1.00	1.00	10.15	3.99
HTD_{8}	Igeo	2.58	3.09	-0.59	0.59	2.76	4.10
HTTD	CF	8.96	12.76	1.00	1.00	10.17	4.10
HTD_9	Igeo	1.95	3.54	-0.59	-0.59	2.76	
HTTD	CF	5.79	17.45	1.00	1.00	10.17	4.00
HTD_{10}	Igeo	0.33	2.60	-0.59	5.55	2.58	- 10
	CF	1.88	9.11	1.00	70.0	8.94	6.40
HTD_{11}	Igeo	-0.26	-6.83	-0.59	7.26	3.25	
HTTD	CF	1.25	0.01	1.00	23.0	14.25	
HTD_2	Igeo	1.02	3.50	6.99	-0.59	2.58	0 = 1
HTD	CF	3.04	17.0	190.0	1.0	8.93	9.74
HTD_3	Igeo	1.31	2.23	-0.59	5.97	2.93	- 1 <i>1</i>
HTD	CF	3.1	7.03	1.0	62.0	11.46	7.14
HTD_{14}	Igeo	-0.10	4.43	-0.59	6.86	2.78	0.50
LIED	CF	1.40	32.37	1.0	174.0	10.29	9.59
HTD_{15}	Igeo	0.69	2.82	-0.59	4.66	2.46	6.02
HTD	CF	2.42	10.58	1.0	38.0	8.26	6.03
HTD_{16}	Igeo	1.58	3.35	7.23	6.12	2.05	16.17
LITE	CF	4.50	5.26	25.0	104.0	6.20	16.17
HTD ₁₇	Igeo CF	0.68	2.88	-0.59	-0.59	2.30	2 97
MTD		2.40	11.00	1.00	1.00	7.39	2.87
MTD_1	Igeo	0.45	2.38	-0.59	6.94	2.37	7.44
MTD_2	CF	2.04	7.82	1.00	184.0 6.91	7.77	7.44
$M1D_2$	Igeo CF	1.35 3.83	3.52 17.18	-0.59 1.00	180.0	2.54 8.70	10.06
MTD		1.55	4.02	4.0	6.30	2.61	10.00
MTD_3	Igeo CF	4.40	24.3	24.0	118.0	9.15	19.43
MTD_4	Igeo	-0.29	1.49	-0.59	5.32	2.66	19.43
$M1D_4$	CF	1.23	4.21	1.0	60.0	9.49	
MTD_5	Igeo	-1.17	3.62	-0.59	5.84	2.29	
W11D ₅	CF	0.67	18.4	1.0	86.0	7.31	6.00
MTD_6	Igeo	1.17	2.41	-0.59	-0.59	2.24	0.00
W11D ₆	CF	3.38	7.97	1.0	1.0	7.33	2.88
LTD ₁	Igeo	0.99	3.45	8.06	6.44	2.17	2.00
LID ₁	CF	2.79	16.34	4.00	140	6.74	28.0
LTD_2	Igeo	-0.29	3.64	8.20	-0.59	2.39	20.0
LID ₂	CF	1.23	18.66	442.0	1.0	7.85	9.5
LTD ₃	Igeo	1.00	1.10	-0.59	5.12	1.99	7.5
	CF	3.00	3.21	1.0	52.0	5.98	4.96
LTD_4	Igeo	0.24	0.26	7.42	5.59	1.75	,0
4	CF	1.77	1.79	256	72.0	5.06	12.6
LTD ₅	Igeo	1.14	4.01	-0.59	5.74	2.48	-2.0
5	CF	3.31	24.18	1.00	80.0	8.36	8.83
LTD ₆	Igeo	-0.10	3.47	-0.59	-0.59	1.91	3.00
0	CF	1.40	16.63	1.00	1.00	5.65	2.65

greater than 1.5 suggests that the source is more likely to be anthropogenic.

The pollution load index (PLI) effectively ranks the pollution status of each site. The PLI values for these sites were greater than 1, indicating deterioration of site quality. Based on PLI values site HTD₆ had the highest pollution load compared to other examined sites.

Principal component analysis. A principal component analysis (PCA) was applied to the data sets and the values are reported in Table 5. PCA provides a means of reducing the complexity of the total metal data sets. Principal component loading values provide information on the relationship among the variables (Meglen, 1992). In this study, PCA was applied to study the correlation among the heavy metals. Three principal components were extracted from dust data set at high traffic density area (Table 5). However, the composition of the factors was different. In dust at high traffic density area, group 1 (or factor 1, expressing about 37.52% of the total variance) includes metals that are mainly from anthropogenic activities (Cd and Pb), group 2 (explaining about 24.91% of the total variance) returned Cu and group 3 (or factor 3, expressing about 20.66 of the total variance) returned Ni alone, which were from anthropogenic activities as well (Knox et al., 1999). The presence of Cd and Pb in the same group for dust at high traffic density area reflects similar behaviour or common source as illustrated in Fig.1. For samples from the low traffic region, PCA results show that two principal components were extracted and accounted for 42.56% and 27.27% of the total variance (Table 5). Group 1 or factor 1 had significant positive loadings in Cr and Pb, respectively. These metals are usually from anthropogenic input (Knox et al., 1999). Group 2 or factor 2 had significant positive loadings in Cu and Cd, which might originate from organic manure, tyres and brake linings as illustrated in Fig.2. Meanwhile, PCA of the heavy metals from the region of medium traffic resulted in one principal component that was extracted. The extraction of one PC reflects similar behaviour or suggests common source (Knox et al., 1999).

Risk assessment. Risk assessment with regards to metal-contaminated dust ingestion was carried out to estimate non-cancer toxic (chronic) risk of the general public including children living in Benin city. Estimation of risk was calculated on the equations detailed in USEPA's Exposure factor Handbook (Hague *et al.*, 2008; Leung *et al.*, 2008; USEPA, 1989). The target

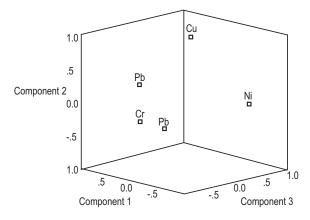


Fig. 1. Component plot in the rotated space for metals in high traffic density area.

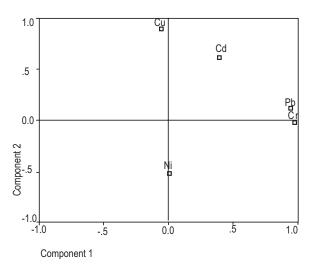


Fig. 2. Component plot in the rotated space for metals in low traffic density area.

hazard quotient (THQ) was determined by the following equation:

$$THQ = \frac{C \times Ing R \times EF \times ED}{BW \times AT \times RFD} \times 10^{-3}$$

where:

C is the mean metal concentration (mg/kg) in dust. Conservative estimates of dust ingestion rate, Ing R, were chose for adult (100 mg/day) and children (200 mg/day). An average body weight, BW, of 60 kg for adults and 15 kg for children. In this study exposure frequency EF = 365 days per year: exposure duration ED = 6 years and the averaging time AT = 2190 days for children and ED = 24 years for adult. RFD is an estimate of daily exposure to human population (including sensitive sub groups) that is likely to be without an appreciable risk of deleterious effect during

Table 5. PCA factor loadings after varimax rotation with Kaiser normalization for dust at high and low traffic
density areas

Metals	High traffic d principal com	•		Low traffic density principal components		
	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	
Cu	-	.927	.186	-	.907	
Cr	_	110	893	.962	-	
Ni	694	-	.529	-	526	
Cd	.642	571	.256	.397	.624	
Pb	.932	-	-	.949	.106	
Var. (%)	37.52	24.91	20.66	42.56	27.27	

Table 6. Estimated target hazard quotient for metals in dust

Metals	High traffic density zor			Medium traffic density zone		ic one
	Adult	Children	Adult	Children	Adult	Children
Cu	0.26	2.05	0.18	1.45	0.16	1.27
Cr	0.03	0.18	0.02	0.17	0.02	0.19
Cd	1.93	15.43	2.40	19.2	2.12	17.0
Ni	1.80	14.38	0.15	1.43	0.24	1.96
Pb	0.07	0.59	0.07	0.54	0.06	0.46
Combined THQ	4.09	32.64	2.82	22.79	2.60	20.88

life time. Therefore, THQ \leq 1 suggests unlikely adverse health effect where THQ > 1 suggests the possibility of adverse health effects. A THQ > 10 is considered to be high chronic risk. It was also assumed that the toxic risks due to metals were additive, therefore the THQ for each metal at the zone scenario was summed to give the combined hazard quotients.

The computed target hazard quotients (THQ) using the mean value for the dust ingest pathway for adult and child scenarios is displayed in Table 6.Of the five metals studied, the THQ for Cd was highest at medium traffic density zone. Generally, the THQ for Cd was highest in all zones (Table 6) for both i.e., adult and child scenarios. In the three zones, the THQ values for Cd spanned between 15.43 and 19.2. There is a high chronic risk of Cd for the child scenarios at all zone since the THQ value > 10.The combined THQ for the metals were greater than 2.60 but less than 4.09 and greater than 20.88 but less than 32.62 for the adult and child scenarios, respectively. The combined THQ for the metals exceeded 1 in all zones which is significant contribution for Cd.

Conclusion

The metals concentration in dust samples of different zones of Benin city, Nigeria were studied from health point of view and metal contamination were higher in all samples except the control site which illustrates high anthropogenic sources at these zones. The distribution and concentration of heavy metals in all studied areas showed that automobile-originated (emissions or by wear and tear of different parts of the car) and emissions from electricity generators and metal fabrication are the main sources of pollution. The levels of metals found in this study were below the USEPA superfund site cleanup goal. The combined THQ value for these metals indicates a long term risk to human from exposure to these metals particularly Cd.

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