IMPACT OF VEHICULAR EXHAUST AND WASTE BURNING ON HEAVY METALS CONCENTRATION IN WAZO MARKET TOPSOIL, OGBOMOSO, NIGERIA

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Abstract: A study of heavy metals levels in Wazo market top soils, Ogbomoso was conducted during dry and rainy season in year 2015 to ascertain status of the soils. Soil samples were collected from five different spots within the market in the month of February, March, June and July. Some physicochemical parameters (pH and total organic carbon) of the soils were determined. The samples were further digested with $HClO_4$, HNO_3 and H_2SO_4 mixture, and digests were analysed for heavy metals using atomic absorption spectrophotometry. The mean levels of heavy metals during the dry season were 249±27.85 mg/kg for Zn, 5.5±1.12 mg/kg for Co, 10±6.00 mg/kg for Cd, 196±60.11 mg/kg for Pb, 14.5±7.63 mg/kg for Ni and 28±6.32 mg/kg for Cu, while during the rainy season the levels of 301±23.88 mg/kg for Zn, 5±0.00 mg/kg for Co, 9±7.87 mg/kg for Cd, 198.5±92.38 mg/kg for Pb, 20.5±8.97 mg/kg for Ni and 45.5±9.76 mg/kg for Cu were observed. The levels of metals based on average concentration during the dry and rainy seasons were Zn >Pb> Cu > Ni > Cd >Co and Zn >Pb> Cu > Ni > Cd >Co, respectively. The average concentration of each metal in the soil during rainy and dry season was almost equal except for zinc and copper which were a bit higher in the wet season. Indices of geo-accumulation revealed that the soils were moderately and strongly contaminated with Pb and Cd respectively. The degree of contamination based on contamination factor showed that the soil can be classified as considerably contaminated with heavy metals during the sampling period. The values of pollution load index obtained during the dry and rainy season indicated that the soil was polluted. In the dry season, at $p < 0.01$, Zn was positively correlated with TOC (0.960). At $p < 0.05$, Pb was negatively correlated with TOC (–0.886) during the dry season while strong correlation exist between Cu-Zn during the rainy season (0.933). This study showed that Wazo market top soil was polluted with heavy metals which may pose serious health challenges on human.

Keywords: Heavy metals, index of geo-accumulation, pollution load index, Wazo market

Introduction

Heavy metals are among the serious pollutants in natural environments due to their toxicity, persistence, non-biodegradable nature and long biological half-lives (Pekey, 2006; Raghunath*et al*., 1999). The natural content of heavy metals in soil is the result of formation factors (the soil type, climate, topography, time of appearance and biota); but their increase may be a result of local and long-range anthropogenic activities such as industrial, agriculture, mining, metallurgical processes and vehicular emission (Malawska and Wilkomirski, 2000).

The pollutants emitted from vehicles get dispersed by wind or rainfall, yet, they reach the soil ecosystem after settling down, since soil are generally regarded as the ultimate sink for heavy metals discharged into the environment (Ata Shakeri *et al*., 2009). A soil may be regarded as being contaminated with heavy metals when the levels of metals found in it are higher than the recommended permissible levels (Giwa *et al*., 2009).

Soils are critical in assessing the potential environmental impacts of automobile emissions and several researchers have indicated the need for a better understanding of heavy metal pollution of roadside soils (De Kimple and Morel, 2000; Manta *et al*., 2002; Tolulope and Taofeek, 2012). Abechi *et al*. (2010) evaluated the contents of heavy metals (Pb, Zn, Mn, Cu, Ni, Cd, Co and Fe) in roadside soils of major streets in Jos metropolis; while Mbah and Anikwe (2010) analyzed variations in heavy metal contents on roadside soils along a major express way in south east Nigeria. The concentrations of heavy metals (Pb, Zn, Cd, Cu, Cr, Co and Ni) in roadside topsoil within Ibadan, Nigeria were also reported by Onianwa (2001). The seasonal variation in the concentration of heavy metals in roadside soil in Yauri, Nigeria was also reported by (Yahaya *et al*., 2010). It was observed that higher heavy metal concentrations were found in the roadside soil during the dry season than in wet season.

The aim of the study was to assess the impact of vehicular emissions from terminal end of Ogbomoso-Ilorin express way and waste burning on the levels of heavy metals in Wazo market topsoil.

Materials and Methods

Description of study area

Wazo market is an agricultural products based market in Ogbomoso, Nigeria. It lies between longitude 4º15'27.61''E and latitude 8º9'56.96''N. It is located along the terminal end of Ogbomoso-Ilorin express way. The market was established ten years ago and provides buyers the opportunity to purchase food items such as maize, beans, rice and perishable goods such as pepper, tomatoes, onions and fruits at cheap and affordable rates.

Sample collections

Soil samples were collected from five different spots in Wazo market with a soil auger and stored in a stainless steel lined with aluminum foil during the dry (February and March, 2015) and rainy seasons (June and July, 2015) making it a total of twenty samples. The samples were air dried at room temperature for 48 h. The samples were then passed through a 2 mm sieve to remove the coarse soil fraction.

Determination of pH

Soil sample (15 g) was weighed into a beaker and 20 ml distilled water added. The suspension was stirred for 15 minutes using a glass rod and allowed to settle for 20 min. The pH meter (Oakton 35423-10 Eco Test pH 2, USA) was standardized using buffer solutions (pH 4 and pH 7). The electrodes of the pH were rinsed with distilled water before each reading. The pH of the various suspensions was recorded digitally by inserting the electrode of the meter into the supernatant (Emmanuel, 2013).

Fig. 1: Location of Wazo market

Determination of total organic carbon

Five grams of the air dried soil samples was weighed into a 100 ml volumetric flask. 10 ml of 0.167 M of $K_2Cr_2O_7$ was added by pipette. 10 ml of concentrated H_2SO_4 was then added and swirled gently. The suspension was allowed to stand on insulating pad for 30 min to avoid rapid heat loss. The suspension was washed with 100 ml of distilled water and filtered to remove suspended particles, three drops of ferroin indicator was then added and the resulting solution titrated with 0.5 M ferrous sulphate solution. As the end point was approached, the solution took on a greenish cast and then changed to dark green at which point ferrous sulphate was added drop by drop until the colour changed rapidly from blue to maroon red. This procedure was then repeated for the remaining samples. The blank titration was carried out. The result of the TOC was calculated according to equation proposed by Adedosu *et al*. (2013).

$$\%\ OrganicCarbon = [(A - B) \times 0.003 \times 100]/C \qquad \text{(i)}$$

Where: A is molarity of $K_2Cr_2O_7$ x ml of solution, B is molarity of FeSO4 x ml of solution, C is mass of air-dry soil (g)

Heavy metals determination

A modified method of Chiroma *et al.* (2012) was used for the digestion of soil samples for heavy metals analysis. One gram each of the air dried soil samples was weighed into a 125 ml beaker and digested with an acid mixture of concentrated $HClO_4$, HNO_3 and H_2SO_4 (4, 25 and 2 ml, respectively), on a hot plate in a fume cupboard. At the end of digestion, the digest was cooled and 50 ml of distilled water was added and then filtered. The filtrate was made up to 100 ml with distilled water and concentrations of the elements were determined using atomic absorption spectrophotometer (Buck Scientific 210VGP AAS).

Assessment of heavy metals contamination

Geo-accumulation index (Igeo)

The index of geo-accumulation (Igeo) is widely used in the evaluation of contamination by comparing the levels of heavy metal obtained to a background levels originally used with bottom sediments (Muller, 1969; Atiemo, 2011). It is calculated using the equation:

$$Igeo = log_2 \frac{C_n}{1.5B_n} \qquad \text{(ii)}$$

Where: Cn is the measured concentration of the heavy metal in soil being studied and Bn is the geochemical background concentration of the heavy metal (crustal average) (Taylor and Meclenan, 1985). The constant 1.5 is introduced to minimize the effect of possible variations in the background values which may be attributed to lithologic variations in the sediments (Lu *et al.*, 2009; Atiemo, 2011).

The pollution load index (PLI)

The Pollution Load Index (PLI) is obtained from contamination Factors (CF). The CF is the quotient obtained by dividing the concentration of each metal by background concentration of metal. The PLI of the place was calculated by obtaining the n-root from the n- CFs that were obtained for all the metals. Generally pollution load index (PLI) as developed by Tomlinson *et al.*, 1980 which is as follows:

$$CF = \frac{C_{metal}}{C_{backgroundvalue}} \qquad \text{(iii)}$$

$$PLI = \sqrt[n]{CF1 \times CF2 \times CF3 \ldots\ldots \times CFn} \qquad \text{(iv)}$$

Where: CF = contamination factor, n = number of metals, C metal = metal concentration in polluted soils, C background value = background value of that metal.

The PLI value of > 1 is polluted, whereas <1 indicates no pollution

Contamination factor and degree of contamination

Contamination factor (C_f) is defined as the single element index. Contamination factor was assessed using the equation below,

$$C_f^i = \frac{C_o^i}{C_n^i} \qquad \text{(v)}$$

WhereC_0 is the mean content of metals from at least five sampling sites and C_n is the pre-industrial concentration. The calculated degree of contamination C_d is defined as the sum of the C_f for the pollutant species specified by Hakanson (1980). C_d was assessed using equation below;

$$C_d = \sum_{i=1}^{n} C_f^i \qquad \text{(vi)}$$

The C_d is aimed at providing a measure of the degree of overall contamination in surface layers in a particular sampling site.

Statistical analysis

The Pearson's correlation coefficient statistical function on SPSS 17 was used to test the relations between heavy metals, pH and TOC.

Results and Discussion

Physicochemical analysis

The pH and TOC of soil collected from the Wazo market are presented in Table 1. The pH ranged from 6.84 - 8.75 with a mean value of 7.74±0.68 during the dry season while it ranged from 7.28 to 8.27 with an average value of 7.66±0.39 during the rainy season. This indicates slight basic conditions for Wazo market topsoil during the sampling period. The percentage of total organic carbon for the soil ranged from 0.22 to 2.59 with a mean value of 1.12±0.38 during the dry season while it ranged from 0.40 to 1.49 with a mean value of 0.81±0.40 during the rainy season. This depicts a moderate total organic carbon in the top soils (Holland *et al.,* 1989).

Table 1: Some physicochemical parameters of Wazo topsoil during the sampling period

Parameters	Dry season	Rainy season
pH	7.74±0.68	7.66±0.39
	(6.84-8.75)	(7.28-8.27)
TOC (%)	1.12±0.38	0.81±0.40
	(0.22-2.59)	(0.40-1.49)

Note: Values in parenthesis are the range during the sampling periods

Concentrations and seasonal variation of heavy metals content

The range and average concentration of different metals in the topsoils of the study area in the two seasons is given in Table 2. The concentration of Zn, Co, Cd, Pb, Ni and Cu in the study area during the dry season ranged from 220-265; 5-6; 5-20; 115-295; 5-25 and 10-50 mg/kg, respectively while it ranged from 215-420 mg/kg for Zn; 5-5 mg/kg for Co; 5-30 mg/kg for Cd;150-420 mg/kg for Pb; 5-25 mg/kg for Ni and 30-60 mg/kg for Cu in the wet season. The trend (in increasing order) of metals according to mean concentration in the dry season and wet season was: Zn >Pb> Cu > Ni > Cd >Co and Zn >Pb> Cu > Ni > Cd >Co respectively. The mean concentrations of Zn in the topsoil during the dry and rainy season were 249±27.85 and 301.5±23.88, respectively. The maximum permissible limit for Zn in soil recommended by WHO/FAO is 300 mg/kg (Chiroma*et al*., 2014). This indicates that Zn concentration levels in the Wazo market soil was below and above the permissible limit during the dry season and rainy season, respectively. The levels of Co, Ni and Cu in the topsoil during the two seasons were below WHO/FAO maximum permissible limit.

The concentrations of Cd in the soil samples during the dry and rainy seasons were 10±6.00 mg/kg and 9±7.87 mg/kg, respectively. The maximum permissible limit for Cd in soil recommended by WHO/FAO is 3 mg/kg (Chiroma *et al*., 2014). This indicates that Cd concentration levels in the Wazo market soil was above the permissible limit during the sampling periods. Cd mean concentration in Wazo market topsoil was also higher compared with 3 mg/kg reported for soil samples from Sabo and General roadside topsoil, Ogbomoso (Taofeek and Tolulope, 2012) and 0.45± 0.12 mg/kg reported for soil samples from high traffic area, Osogbo (Fakayode and Olu-owolabi, 2003). This might be from vehicular emission as Nigeria has witness the impetration of sub-standard quality petroleum products in recent times. This is worrisome, because cadmium has been linked with the damage of lungs, kidneys and bones, and it is a known human carcinogen. Its toxicity is linked with reproduction problem because it affects sperm and reduces birth weight (Olawoyin *et al.,* 2012).

The concentrations of Pb in the soil samples during the dry and rainy season were 196±60.11mg/kg and 198.5±92.38 mg/kg, respectively. The concentration of Pb in the soil samples during the sampling periods was above the WHO/FAO maximum permissible limit (100 mg/kg) (Chiroma *et al*., 2014). Pb mean concentration observed in Wazo market topsoil was also higher compared to Pb level of 10 mg/kg in Sabo and General roadside soil Ogbomoso (Taofeek and Tolulope, 2012) and 63.69±27.31 mg/kg reported for Osogbo at 5 m from road side (Fakayode and Olu-Owolabi, 2003). The elevated concentrations of Pb and Cd could be attributed to the terrain (roundabout) of Ogbomoso-Ilorin express road at Wazo market in which all vehicles have to reduce their speed to the lowest point. This would enhance higher discharge of exhaust gas deposited at Wazo market topsoil. Lead affects the brain, causing hyperactivity and deficiency in the fine motor functions, thus, it results in damage to the brain (Emmanuel, 2013).

Pb and Cd may pose some environmental challenges in Wazo market since their mean concentrations exceeded the maximum permissible limit. This might have serious effects on the health of Wazo market merchants because they are exposed to dust particles in the market by inhalation.The average concentrations of metals in the topsoil during wet and dry season were almost the same, except for Zn and Cu which were a bit higher in the wet season.

Table 2: Concentration of heavy metals compared with WHO/FAO limit (Chiroma *et al*., 2014)

Heavy metals	Present study (mg/kg)		Maximum permissible limit in soil (mg/kg)
	Dry season	Rain season	
Zn	249±27.85	301.5±23.88	300
	(220-265)	(215-420)	
Co	5.5±1.12	5±0.00	50
	(5-6)	(5-5)	
Cd	10±6.00	9±7.87	3
	(5-20)	(5-30)	
Pb	196±60.11	198.5±92.38	100
	(115-295)	(150-420)	
Ni	14.5±7.63	20.5±8.97	50
	(5-25)	(5-35)	
Cu	28±6.32	45.5±9.76	100
	(10-50)	(30-60)	

Note: Values in parenthesis are the range of metals during the sampling period

Table 3 Geo-accumulation index for studied heavy metals in Wazo market topsoil

Soil sample	I-geo Zn	I-geo Co	I-geo Cd	I-geo Pb	I-geo Ni	I-geo Cu
Dry season	- 0.3	- 3.0	3.0	0.4	- 2.0	- 2.0
Rainy season	0	-3.2	2.6	0.4	-1.5	-1.3

Interpretation: The following classification is given for geo-accumulation index (Muller, 1969; Huu *et al.*, 2010; Atiemo, 2011). I-geo <0 = practically unpolluted, 0-1 = unpolluted to moderately polluted, 1-2 = moderately polluted, 2-3 = moderately to strongly polluted, 3-4 = strongly polluted, 4-5 = strongly to extremely polluted and >5 = extremely polluted

Geo-accumulation index (I-geo)

As shown in Table 3 I-geo values for Zn, Co, Ni, and Cu were found to be less than zero. This shows that the concentrations of Zn, Co, Ni and Cu did not reach the contamination levels during the dry and rainy season. I-geo values for Pb fell into the class of uncontaminated to moderately contaminated, since its I-geo value was 0.4 during the dry and rainy season, while the I-geo values obtained for Cd in Wazo market topsoil fell into the class of moderately to strongly contaminate during the sampling period. The values of I-geo increased in the order of Co < Ni = Cu < Zn <Pb<Cd in the dry season while its increased in the order of Co < Ni < Cu < Zn <Pb<Cd in the rainy season.

Contamination factor (CF), the degree of contamination (CD) and pollution load index (PLI)

From Table 4, it is observed that the contamination levels for Co, Cu and Ni in Wazo market topsoil were low while they were moderate for Zn and Pb .The contamination levels for Cd in Wazo topsoil was high during the rainy and dry season. The contamination factor increases in the order Co < Ni = Cu < Zn <Pb<Cd and Co < Ni < Cu < Zn <Pb<Cd for dry and rainy season respectively. The degree of contamination based on contamination factor indicated that the soil can be classified as considerably contaminated. Pollution load index indicated that Wazo market topsoil is polluted with heavy metals. Estimation of impact of pollution by metals in the soil during rainy and dry season showed less variation.

Table 4: Contamination factor (CF), the degree of contamination (CD) and pollution load index (PLI) for metals in the topsoil of Wazo market

Period	Contamination Factor						CD	PLI
	Zn	Co	Cd	Pb	Ni	Cu		
Dry season	1.3	0.2	10	2.0	0.4	0.4	14.3	1.0
Rainy season	1.5	0.2	9	2.0	0.5	0.6	13.8	1.1

Interpretation: CFs value< 1 indicate low contamination, those in the range of 1-3 – moderate contamination, 3-6 – considerable contamination, and >6 very high contamination. CDs values below 5 indicate low contamination, 5-10 – moderate contamination, 10-20 – considerable contamination and 20<CD very high contamination. Håkanson (1980); Interpretation: PLI< 1= no pollution, PLI >1= pollution. Muller (1969)

Correlation matrix

Pearson correlation analysis (Edward, 1976) was performed between all the variables in Wazo market top soils. The levels of significance ($p < 0.05$ and $p < 0.01$) of multi-element correlation, pH and total organic carbon for soil samples were determined and the results are given in Table 5a and 5b. The inter-metallic correlation coefficients in the soil samples with $p < 0.05$ during dry and rainy season were: Ni-Zn, and Cu-Zn respectively. In the dry season, Zn was positively correlated with TOC (0.960) at $p < 0.01$ while Pb was negatively correlated with TOC (-0.886) at $p < 0.05$. This suggests the value of TOC will favour increase and decrease in concentration of Zn and Pb respectively during the dry season. Very strong correlation exists between Cu-Zn (0.933) during the rainy season. The significant correlations indicate that they may have originated from common sources, presumably from anthropogenic (smoking of tobacco, indiscriminate burning of waste and vehicular emission) activities.

Table 5a: Pearson correlation coefficient (r) of individual heavy metals, pH and TOC in soil during the dry season

Metal	Zn	Co	Cd	Pb	Ni	Cu	pH	TOC
Zn	1	nd	-0.030	-0.760	-0.943*	0.540	-0.464	0.960**
Co		nd	nd	Nd	nd	nd	nd	nd
Cd			1	-0.546	-0.029	-0.783	0.054	0.149
Pb				1	0.647	0.022	0.160	-0.886*
Ni					1	-0.470	0.591	-0.862
Cu						1	-0.030	0.427
pH							1	-0.256
TOC								1

nd- not detected; *-correlation is significant at the 0.05 level (2-tailed); **-correlation is significant at the 0.01 level (2-tailed)

Table 5b: Pearson correlation coefficient(r) of individual heavy metals, pH and TOC in soil during the rainy season

Metal	Zn	Co	Cd	Pb	Ni	Cu	pH	TOC
Zn	1	nd	-0.567	-0.768	0.412	0.933*	0.619	0.338
Co		nd	Nd	Nd	Nd	nd	nd	Nd
Cd			1	0.568	0.431	-0.590	-0.107	-0.362
Pb				1	0.061	-0.511	-0.682	0.271
Ni					1	0.461	0.411	0.322
Cu						1	0.392	0.655
pH							1	-0.295
TOC								1

nd- not detected, *-correlation is significant at the 0.05 level (2-tailed).Correlation rating: > 0.91 = very strong, 0.90 – 0.81 = strong, 0.80 – 0.31 = moderate, < 0.30 = weak

Conclusion

Concentrations of all heavy metals analyzed in this study showed the same trend during the rainy and dry seasons except for Zn and Cu which were a bit higher in the rainy season. Pb and Cd were above maximum allowable limit during the sampling periods. Although, this may be taken as a preliminary one, but the high levels of Pb and Cd which may pose some health risks, call for a comprehensive and regular surveillance of these heavy metals in the soil of this market. Correlation analysis carried out on heavy metals, pH, TOC indicates positive correlation between some metals indicating same source. Pollution load index estimated based on the analysis of some heavy metals in the topsoil of Wazo market, Ogbomoso, Nigeria during the rainy and dry seasons of 2015 showed that the soil was polluted with some heavy metals during the periods of analysis. Index of geo-accumulation results revealed that the study area was moderately and strongly contaminated with Pb and Cd, respectively. Analysis based on contamination factor, showed that soil can be classified as moderately contaminated with Zn, and Pb; and highly contaminated with Cd. The degree of contamination based on contamination factor showed that the soil can be classified as considerably contaminated during the dry and rainy season. The pollution sources in Wazo market topsoil are due to vehicular exhaust along Ilorin-Ogbomosho axis and burning of waste within the market environment. The accumulation of these pollutants in the topsoil may pose serious effects on the health of market merchants and could leach to groundwater and runoff into nearby surface water bodies around the area.

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