JJEES

Volume 7, (Number 1), June, 2015
ISSN 1995-6681
Pages 49 - 63

Jordan Journal of Earth and Environmental Sciences

Concentrations, Human and Ecological Risks of Metals in Soils in the Vicinity of Asphalt Plants in Delta States, Nigeria

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Received 14 February, 2014; Accepted 31 March 2015

Abstract

The concentrations of metals, cadmium (Cd), lead (Pb), chromium (Cr), nickel (Ni), copper (Cu), cobalt (Co), iron (Fe), manganese (Mn) and zinc (Zn) were measured in soil profiles in the vicinity of asphalt plants in Delta State, Nigeria by atomic absorption spectrometry after acid digestion. The concentrations of the metals in all depths and distances from the asphalt plants ranged from 0.07 to 0.58 mg kg^{-1} for Cd; 37.1 to 177 mg kg^{-1} for Cr; 2.0 to 31.1 mg kg^{-1} for Cu; 2.0 to 11.1 mg kg^{-1} for Co; 20 to 143 mg kg^{-1} for Ni. The concentrations of metals in these sites were below the Department of Petroleum Resources' maximum allowed values of metals in soils, except for Ni and Cr. The estimated contamination/pollution index indicates that the examined sites fall into slight to severe pollution ranges with a significant contribution from Cr and Ni. The total ecological risk (RI) values of metals in these soil profiles were <150 which suggested low ecological risks for these soils. However, the total cancer risk of metals in these soil profiles exceeded the target value of ($1/10^6$) one in a million chance of developing cancer.

Keywords: Heavy metals; Soil contamination; Asphalt plants; Nigeria.

1. Introduction

Anthropogenic emissions, arising from agricultural development, industrialization and urbanization, have become the major sources of soil contamination by metals. The soil acts as a geochemical reservoir and a natural medium for the transportation and the redistribution of contaminants in the biomass, terrestrial and aquatic environments (Behaddya and Hadjel, 2014). Metals are of environmental and human health concerns because (i) they exhibit a wide range of toxicity and chronic health effects such as cancer, reproductive, developmental and neurological disorders, cardiovascular, kidney and renal problems, lung damage, contact dermatitis, and brittle hair and hair loss. Many are suspected endocrine disruptors and respiratory toxin; (ii) they are resistant to degradation under natural terrestrial surface conditions; and (iii) they are discharged into the environment through a range of natural and anthropogenic processes (Lieben et. al., 2012). Metals may accumulate rapidly in soils but they may be removed from soils through leaching, plant uptake, erosion or deflation very slowly, requiring times of centuries or even millennia. Such persistent contaminants in soil make soil pollution much more serious than air or water pollution. Soil contamination affects every other components of the environment including food chain, namely plants, grazing animals and, ultimately, man (Itana, 1998).

Road construction is one of the strategic priorities of economic, social and political development in every country. In Nigeria, the need for road construction and rehabilitation is urgent because of the bad quality of roads and the increasing traffic density. The number of asphalt plants established is increasing as the need for the construction of these roads increases year by year. These asphalt plants continuously emit particles into the atmosphere; such emissions may contaminate air, soil and surface water as well as groundwater. Particulate matters have devastating effects on plants when directly absorbed through the leaves. Absorption of dust through the leave stomata lead to destruction of the chlorophyll and retardation of plant growth (Maina et. al., 2009).

Studies on the impact of various industrial discharges on the metal concentrations of soils in Nigeria have been documented, e.g., battery (Onianwa and Fakayode, 2000) fertilizer (Aina and Srhida, 2004), oil and gas (Iwegbue et. al., 2006) and cement industries (Maina et. al., 2009). However, relatively little or no information is currently available on the concentrations and distribution of metal in soils close to the asphalt plants in Nigeria, although Iwegbue (2013) provided information on the chemical fractionation and mobility patterns of metals in these soil profiles. The objective of the present study was to determine the concentrations of metals, Cd, Pb, Zn, Ni, Cr, Mn, Fe, Cu and Co, in soils in the vicinity of asphalt plants with a view of providing information on the extent of contamination, human and ecological risks associated with discharges from these plants.

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2. Materials and Methods

Soil samples were collected from five asphalt plants at different locations in Delta State (Fig. 1). At each site, soil samples were collected at immediate vicinity of asphalt plants) and at 500 m distance from the plant in the windward direction. At each distance, at least 10 random samples were collected at different depths (0-15, 15-30 and 30-60 cm), using a 150 m stainless steel auger. Samples collected at a given depth and distance were mixed together to form composite samples. The soil samples were air dried and sieved to pass through 2 mm mesh sieve. The soil pH was determined in soil water suspension (1:2.5 soil: water ratio) by using glass electrode (Abollino et. al., 2002). The electrical conductivity of the soil was determined on the filtrate obtained from filtering the suspension used for pH determination by using conductivity meter. Total organic carbon was determined by the wet dichromate method as described by Radojevic and Bashkin (1999).

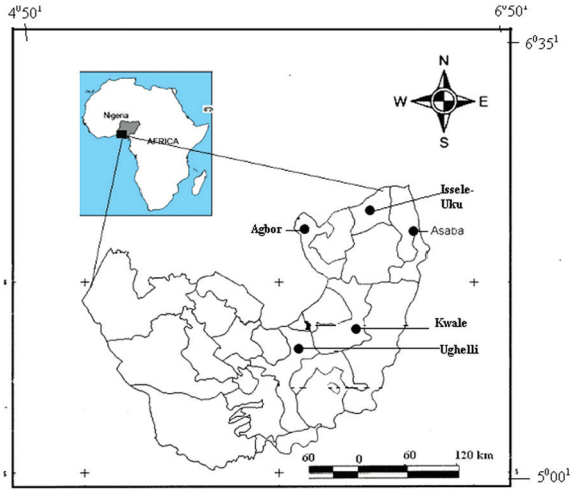

Figure 1. Map of Delta State showing the Study Areas.

A 1.0 gram sample of the soil sample was placed in a digestion tube, followed by the addition of 15 mL of aqua regia (3:1 HCl: HNO_3) and was then swirled to wet the sample and allowed to stand overnight. The following day, the tube was heated in a heating block of 50 ^oC for 30 min. and raise to temperature of 120 ^oC for 2 h. The digest was cooled to room temperature, the cover of the digestion tube was rinsed with 0.25 mol/L HNO_3 into the digest and filtered through Whatman No1 filter and made up to 25 mL with 0.25 mol/L HNO_3 (Radojevic and Bashkin, 1999). The sample solutions were analysed for Cd, Pb, Ni, Cr, Cu, Co, Fe, Mn and Zn by using atomic absorption spectrometry (Buck Model 205) equipped with D_2 background correction devices.

Reagent blank of the digestion process was analysed with each batch of 10 samples. The acids used for digestion were of analytical grades. Calibration standards for atomic absorption analysis were prepared by diluting a commercial Merck standard solutions of the metals (1000 mg/L) with 0.25 M HNO_3 to closely matching the matrix of diluted digest. Each sample was analysed in triplicates and the coefficient of variations between the triplicates analyses were less than 8% in all for metals. The quality control was assured by the use of blanks and spike recovery method. The average bland reading was used to correct all instrument readings. The procedure was validated by introducing known standards of the studied metals at three concentration levels into fresh portions of the sample and repeating all analysis steps from digestion to atomic absorption analysis. The spike recoveries for the various metals were within 100% $\pm$ 10%.

Contamination/pollution index (C/PI): This provides adequate information about the significance of the measured concentrations of metals on the intrinsic soil features and how the values obtained are related to the maximum allowable limits for the metals (Iwegbue et. al., 2010). The contamination/pollution index was computed as a ratio of metal concentration measured by chemical analysis to reference value. The contamination/pollution index was derived by employing the contamination/pollution index as defined by Lacutusu (2000):

$$C/PI = \frac{\text{Concentration of metal in soil}}{\text{Reference value}} \quad (1)$$

The reference value in this case is the Department of Petroleum Resources of Nigeria maximum allowable levels of metals in soil (DPR 2002) (Table 1). The conversion formula used for the C/P index varies from one country to another based on the chosen criteria. C/P index value greater than unity (1) defines the pollution range and when the value is less than unity defines the contamination range. The presence of one metal can significantly affect the impact that another has on organisms. This effect can be synergistic, additive or antagonistic, this reason, the multiple pollution index (MPI) is derived by the addition of the C/PI values for individual metals greater than 1. The computed C/P index and multiple pollution index (MPI) values were interpreted according to the scheme provided in below. The categorization of degree of contamination/pollution based on this index is as follows; <0.1 = very slight contamination; 0.10-0.25 = slight contamination; 0.26-0.5=Moderate contamination; 0.51-0.75 = Severe contamination; 0.76-1.00 = very severe contamination; 1.1-2.0 = slight pollution. 2.1-4.0 = moderate pollution; 4.1-8.0 = severe pollution; 8.1-16.0 = very severe pollution; >16.0 = excessive pollution.

Table 1: Some international environmental guidelines for metals in soils (mg kg^{-1})

Metal	Assessment Criteria						
	DTV	AEIL	EC	CEQC	DPR	Crustal abundance value	Shale[a]
Cd	0.8	3	3.0	0.5	0.8	0.11	0.3
Cr	100	400	-	20	100	100	90
Cu	36	100	140	30	36	50	45
Ni	35	60	75	20	35	80	68
Pb	85	600	300	25	85	14	20
Zn	140	100	300	60	140	75	95
Co	20		-		20	20	19
Mn						950	850
Fe						4.1*	4.7*

*value in (%)
[a]Wedephl and Turekien, 1961

Quantification of Enrichment Factor (EF): The enrichment factor was computed using the expression:

$$EF = \frac{\frac{C_n\ (Samle)}{C_n\ (reference)}}{\frac{B_n\ (test\ elements)}{B_n\ (reference)}} \quad (2)$$

where

Cn (Sample) = concentration of the test element in the sample

Cn_{ref} = Concentration of the reference element in the sample

Bn test element = background concentration of the test element in crustal rock

Bn_{ref} = background concentration of the reference element in crustal rock (Reimann and De Caritat, 2000).

In this case, iron was chosen as the reference element because it is the most abundant element in the earth crust. The crustal abundance values for the respective metals (Turiekian and Wedepohl, 1961) are used for the estimation of the enrichment factors (Table1). Five contamination categories are recognized on the basis of the enrichment factor (Sutherland, 2000; Loska and Wiechula, 2003). 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.

Geoaccumulation index (Igeo): The index of geoaccumulation is useful for comparing the current and pre-industrial concentrations of metals in bottom sediments (Muller, 1969). It has also been applied in the assessment of the extent of soil contamination. The geoaccumulation index is given by the equation:

$$Igeo = \text{Log } 2\ \frac{C_n}{1.5B_n} \quad (3)$$

where Cn is the measured concentration of the element and Bn is the background concentration. In this case, the background concentration is the crustal abundance values of the respective metals (Table 1) (Turiekian and Wedepohl, 1961). Factor 1.5 is applied because of the possible variations in the background values due to lithological variations (Rogan et. al., 2010). The Muller index has seven classes depending on its value: <0 or 0 no pollution, values from 0 to 1, not polluted to moderately polluted (class 1); 1-2, moderately polluted (class 2); 2-3, moderately polluted to polluted (class 3); 3-4, polluted to strongly polluted (class 4); 4-5, strongly polluted (class 5); 5-6, strongly polluted to very polluted (class 6); and >6, very polluted (class 7).

Statistical Analysis: Two-way analysis of variance (ANOVA) and student's t test were used to determine whether the concentrations of metals varied significantly between sampling sites, depths and distance, with values less than 0.05 ($p<0.05$) considered statistically significant. The relationship between the metals was established by means of principal component analysis. The statistical calculations were performed with SPSS 20.1 version (SPSS Inc, Chicago IL, USA).

2.1. Ecological risk assessment

The index of evaluating ecological risks of metals was originally introduced by Hakanson (1980). This index has been used for ecological risk assessment of metals in sediments, soil and dusts (Saeedi et. al., 2012). The potential ecological risk index is given by the equation:

$$RI = \Sigma\ Er \quad (4)$$

$$\text{where } Er = Tr \times CF \quad (5)$$

$$CF = Cs / Cn \quad (6)$$

where CF= contamination factor which a ratio of metal concentration in the sample (Cs) and that of the background (Cn). Also, the background concentrations used are the crustal abundance values of the respective metals (Turiekian and Wedepohl, 1961).

Er and RI are the ecological risks of each metal and that of multiple metals, respectively.

Tr is the toxic response factor for the given element. The toxic response factors for Cd, Cu, Pb, Cr and Zn were 30, 5, 5, 2 and 1, respectively (Hakanson, 1980). The Er and RI have been classified into five and four categories depending on their values, respectively. Er value <40 denotes low potential ecological risk; ≥40<80 moderate potential ecological risk; ≥80<160 considerable potential ecological risk; ≥160<320 high potential ecological risk and ≥320 very high potential ecological risk. RI value <150 indicates low ecological risk; ≥150<300 moderate ecological risk; ≥300<600 high ecological risk and ≥600 very high ecological risk (Hakanson, 1980).

2.2. Human exposure and health risk assessment

Humans can be exposed to metals in soil through three pathways which include direct ingestion of soil, inhalation of particulates emitted from soil and dermal absorption of metals through soil adhered to exposed skin (Shi et. al., 2014; Lai et. al., 2010). The non-carcinogenic and carcinogenic risk of these exposure pathways were considered in this study. The non-carcinogenic hazard risk (HI) for children and adults was calculated using equations (7)-(12) adapted from USDOE (2011) and USEPA (2001; 2011):

$$CDI_{ing\text{-}nc} = \frac{C \times IngR \times EF \times ED}{BW \times AT_{nc}} \times 10^{-6} \quad (7)$$

$$CDI_{inh\text{-}nc} = \frac{C \times EF \times ET \times ED}{PEF \times 24 \times AT_{nc}} \quad (8)$$

$$CDI_{derma\text{-}nc} = \frac{C \times SA \times AF \times ABSd \times EF \times ED}{BW \times AT_{nc}} \times 10^{-6} \quad (9)$$

$$\text{Hazard Quotient (HQ)} = \frac{CDI_{nc}}{RfD} \quad (10)$$

$$\text{Hazard index (HI)} = \sum HQ = HQ_{ing} + HQ_{inh} + \text{HQ dermal} \quad (11)$$

$$\text{Hazard index (HI)} = \frac{CDI_{ing}\ -nc}{RfD_{ing}} + \frac{CDI_{inh}\ -nc}{RfC_{inh}} + \frac{CDI_{dermal}\ -nc}{RdDermal} \quad (12)$$

The carcinogenic risk was calculated for the life time exposure, estimated as the incremental probability of an individual developing cancer over a lifetime as a result of total exposure to the potential carcinogens (Cd, Cr, Ni and Pb). The carcinogenic hazard risk (Total Risk) for children and adult was calculated using equation (13)-(20) adapted from USDOE (2011):

$$CDI_{ing\text{-}ca} = \frac{C \times IngRadj \times EF}{ATca} \times 10^{-6} \quad (13)$$

$$IngR_{adj} = \frac{ED_{child} \times IngR_{child}}{BW_{child}} + \frac{(ED_{adult} - ED_{child})}{BW_{adult}} \times IngR_{adult} \quad (14)$$

$$CDI_{inh}\text{–ca} = \frac{\text{C x EF x ET x ED}}{} \times 10^{3} \quad (15)$$

$$CDI_{dermal}\text{–ca} = \frac{\text{C x ABSd x EF x DFSadj}}{} \times 10^{-6} \quad (16)$$

$$DFS_{adj} = \frac{ED_{child} \times SA\ child \times AF\ child}{BW_{child}} + \frac{(ED_{adult} - ED_{child}) \times SAadult \times AF\ adult}{BW_{adult}} \quad (17)$$

$$Risk = CDI_{ca} \times CSF \quad (18)$$

$$Total\ Risk = Risk_{ing} + Risk_{inh} + Risk_{dermal} \quad (19)$$

$$Total\ Risk = CDI_{ing}\text{–ca} \times CSF_{ing} + CD_{inh}\text{-ca} \times IUR + \frac{CDI_{dermal} \times CSF_{ing}}{ABS_{GI}} \quad (20)$$

where CDI_{ing}, CDI_{inh}, CDI_{dermal} are the chronic daily intake or dose contacted through ingestion, inhalation and dermal contact with soil, respectively. RfD is the reference dose, RfD_{ing} (chronic oral reference dose), RfC_{inh} (chronic inhalation reference concentration), RfD_{dermal} (chronic dermal reference dose = RfD_{ing} x ABS_{GI}) through the three exposure pathway, respectively. CSF_{ing} is chronic oral slope factor via ingestion, IUR is the chronic inhalation unit risk, CSF_{dermal} is chronic dermal slope factor = CSF_{ing}/ABS_{GI} and C is the concentration of metals in soil. The definitions of the symbols and values for Nigerian-specific variables are displayed in Table 2 while the toxicological parameters of the investigated metals used for health risk assessment are displayed in Table 3.

Table 2: Values of variables for estimation of human health risk assessment

Parameters	Unit	Definition	Values		References
			Child	Adult	
C	µg/g	Metals concentration in soil			
ABS_d	-	Dermal absorption factor	0.03	0.001	USEPA, 2011
AF	mg/cm^2	Soil to skin adherences factor	0.2	0.07	USEPA, 2011
BW	Kg	Average body weight	15	60	
ED	Year	Exposure duration	6	24	USEPA, 2001
EF	d/yr	Exposure frequency	313	313	Man et. al. (2013)
ET	h/d	Exposure time	8	8	USEPA, 1987
IngR	mg/d	Soil ingestion rate for receptor	200	100	USEPA, 2001
SA	cm^2/event	Skin surface area	2800	5700	USEPA, 2001
ATnc	D	Averaging time for non-carcinogenic	ED x 365		USEPA, 1997
ATca	d	Averaging time for carcinogenic	LT x 365		USEPA, 1997
DFS_{adj}	mg/yr/kg/d	Soil dermal contact for-age-adjusted	110		Equation (14)
$IngR_{adj}$	mg/yr/kg/d	Soil ingestion rate-age adjusted	344		Equation (11)
LT	Year	Lifetime	48.9		
PEF	m^3/kg	Soil to air particulate emission factor	1.36×10^9		USDOE, 2011

Table 3: Toxicological parameters of the investigated metals used for health risk assessment

Element	CSF_{ing} (mg/kg/d)	IUR (µg/m^3)	RfD_{ing}	RfC_{inh}	ABS_{GI}
Cd		1.8×10^{-3}	1.0×10^{-3}	1.0×10^{-5}	0.025
Cr	5.0×10^{-3}	1.2×10^{-2}	3.0×10^{-3}	1.0×10^{-4}	0.013
Ni		2.6×10^{-4}	2.0×10^{-2}	9.0×10^{-5}	0.04
Fe			7.0×10^{-1}		1
Zn			3.0×10^{-1}	$4.0 \times 10^{-3*}$	1
Co			3.5×10^{-3}	6.0×10^{-6}	1
Pb	8.5×10^{-3}	1.2×10^{-5}	1.4×10^{-1}	$2.0 \times 10^{-4*}$	1
Mn			4.0×10^{-1}	5.0×10^{-5}	1
Cu				1.4×10^{-3}	1
Reference	USDOE, 2011	USDOE, 2011	USDOE, 2011	USDOE, 2011	USEPA, 2011

*MOEE, 2008

The qualitative description of human health risk assessment followed that HQ value above 1 suggests the level of concern. That is, HQ ≤ 1 suggested unlikely adverse health effects whereas HQ > 1 suggested the probability of adverse health effects (Luo et. al., 2012a). In general, the total cancer risk lower than 10^{-6} (a probability of 1 chance in 1,000,000 of an individual developing cancer) are considered to be negligible and cancer risks above 10^{-4} are considered unacceptable by most international regulatory agencies (US EPA, 1989; Guney et. al., 2010; Luo et. al., 2012a). The value 10^{-6} is also considered the carcinogenic target risk (US EPA, 2011; Luo et. al., 2012a).

3. Results and Discussion

The results of some physicochemical characteristics and concentrations of metals in soils within the asphalt plants and at 500 m distance from the plants are displayed in Table 4. The soil pH ranged from 6.5 to 8.2. The soil pH decreased with increasing depth. The soil pH, cation exchange capacity and organic matter are some of the factors that control the availability, retention and mobility of metals. The electrical conductivity of the examined soil samples ranged from 21.6 to 246.1 µScm^{-1} for all sites and depths. The conductivity of the examined soils corresponds to the values reported for some

soil types in southern Nigeria (Iwegbue et. al., 2006; Iwegbue et. al., 2009). Total organic carbon and soil conductivity decreased with increasing depth of the soil profile. The total organic carbon (TOC) values ranged from 0.3 to 0.9%. The total organic carbon contents of the topsoil for the different sites showed no significant difference ($p>0.05$).

Table 4: Physicochemical characteristics and total metal concentrations (mg kg^{-1}) in soils within the plants and 500 m distance from the Asphalt plant

		Within the Asphalt plant					500 m distance from the Asphalt plant				
Parameter	**Depth (cm)**	**I**	**II**	**III**	**IV**	**V**	**I**	**II**	**III**	**IV**	**V**
pH	0-15	8.2	6.8	7.9	8.2	7.9	7.8	7.5	7.4	7.6	7.1
	15-30	6.9	8.2	6.5	7.6	6.5	6.9	6.7	6.5	7.8	6.4
	30-60	7.1	7.8	6.5	6.7	6.9	7.4	6.9	7.3	6.4	6.8
Conductivity (µS cm^{-1})	0-15	246	211	232	197	212	124	196	129	99.7	97.7
	15-30	134.7	139	143	142	135	86.5	78.3	76.7	10	78.3
	30-60	117	59.0	21.6	112	66.0	55.7	51.5	52.0	49.3	61.7
TOC (%)	0-15	0.9	0.9	0.9	0.8	0.8	0.6	0.6	0.6	0.6	0.5
	15-30	0.5	0.3	0.7	0.5	0.4	0.3	0.4	0.4	0.4	0.6
	30-60	0.5	0.5	0.6	0.3	0.3	0.2	0.2	0.2	0.3	0.3
Cd	0-15	0.3	0.4	0.3	0.3	0.3	0.2	0.2	0.1	0.2	0.1
	15-30	0.2	0.3	0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.1
	30-60	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Pb	0-15	3.5	4.1	3.0	3.1	3.0	2.0	2.8	1.7	1.5	1.4
	15-30	1.0	2.0	2.1	1.5	1.6	1.2	1.0	1.0	1.0	1.6
	30-60	0.9	1.1	1.0	1.0	1.0	1.0	0.9	0.9	0.7	0.6
Ni	0-15	115	119	12	143	138	65.0	131	96.1	76.9	69.8
	15-30	87.9	107	106	120	113	42.1	126	72.1	37.3	74.7
	30-60	63.0	91.3	59.1	97.6	93.8	38.0	103	105	21.1	20.1
Cr	0-15	156	150	165	176	166	96.8	88.4	107	89.8	102
	15-30	12.4	189	147	149	150	61.1	60.1	55.7	56.3	87.6
	30-60	9.0	12.0	9.1	121	126	50.2	49.5	50.1	37.1	41.7
Cu	0-15	28.8	31.1	26.1	10.1	12.3	19.1	28.1	9.0	6.0	12.0
	15-30	12.4	10.7	21.0	6.2	8.0	7.3	12.4	11.1	4.1	5.7
	30-60	9.7	9.0	10.4	2.0	4.7	4.3	9.9	10.0	2.0	1.9
Co	0-15	8.6	10.1	10.1	11.1	9.8	6.4	6.6	7.4	6.8	7.0
	15-30	4.2	9.8	8.6	6.2	1.8	4.0	4.1	3.1	4.1	6.0
	30-60	2.2	4.0	2.0	4.0	2.0	2.0	2.0	2.0	2.2	2.0
Fe	0-15	257	257	231	224	243	188	123	129	170	151
	15-30	98.4	101	113	108	116	89.7	67.3	90.7	86.3	89.0
	30-60	78.4	86.1	81.7	77.9	81.5	68.1	59.0	58.0	62.9	71.3
Mn	0-15	183	278	165	151	194	162	151	74.1	70.4	91.5
	15-30	71.6	74.0	76.3	69.9	85.0	87.0	56.2	69.7	62.6	63.4
	30-60	56.1	61.1	60.7	54.1	61.4	47.0	43.1	42.3	48.0	55.0
Zn	0-15	101.8	32.0	100.0	50.2	60.7	92.9	89.9	46.9	41.3	42.2
	15-30	65.1	80.8	79.5	43.1	41.3	56.8	61.0	56.1	27.0	39.9
	30-60	52.1	60.1	58.9	32.1	36.1	48.8	49.7	50.1	21.2	1.0

The concentrations of metals in the investigated soils decreased with respect to the depths and the distance from the asphalt plants. The concentrations of metals observed in soil profiles within the asphalt plants were higher than the concentrations of metals observed in soils collected at 500 m distance from asphalt plants. The differences observed in the concentrations of metals at these sites were significant ($p<0.05$), except for Cd. The concentrations of metals in the studied soils were compared with crustal abundance values, national and international guidelines for metals in soil (Table 1). The concentrations of the examined metals were below their respective crustal abundance values except for Cd, Cr and Ni.

The concentrations of Cd ranged from 0.1- 0.4 mg kg^{-1} and from 0.1 - 0.2 mg kg^{-1} within the plant areas and 500m away from the asphalt plant, respectively. The maximum allowable concentration of Cd in soil is 0.8 mg kg^{-1} (DPR, 2002). The concentrations of Cd observed in these soil profiles were below the maximum allowable concentration. Dudka et. al. (1996) reported Cd levels in arable soil in industrial area of Upper Silesia, South Poland to be 3.2 $mgkg^{-1}$ while Umoren and Onianwa (2005) reported concentrations in the range of 1.7-23 mg kg^{-1} Cd in soils around urban industrial area in south western, Nigeria. Similarly, Inuwa et. al. (2007) found

Cd levels of 0.10-0.70 mg kg^{-1} in soils of major industrial areas of north-western Nigeria. The concentrations of Cd found in these soil profiles are comparable to the levels of Cd in soils reported by Inuwa et. al. (2007).

The concentrations of Pb in these soil profiles ranged from 0.9 - 4.1 mg kg^{-1} and from 0.6 - 2.8 mg kg^{-1} within the asphalt plants and 500 m distance from the plants, respectively. The highest concentration of Pb was observed in site II. The maximum allowable concentration of Pb in soil in Nigeria is 85 mg kg^{-1} (DPR, 2002). The concentrations of Pb found in these soil profiles were lower than the maximum allowable concentrations. The concentrations of Pb observed in these sites were lower than the concentrations of Pb observed in soils around some industrial sites in Nigeria (Iwegbue et. al., 2006; Iwegbue et. al., 2009 b; Maina et. al., 2009) and India (Krishna and Govil, 2008).

The concentrations of Ni in these soil profiles varied from 59.1-143 mg kg^{-1} within the plants premises, and from 20.1-131 mg kg^{-1} at 500 m distance from the asphalt plants. The concentrations of Ni in the soil profile of site IV were higher than that of the other sites. The concentrations of Ni in these soil profiles exceeded the Department of Petroleum Resources of Nigeria permissible limit of 36 mg kg^{-1} (DPR, 2002) except for the soils collected from the 30 – 60 cm depth of sites IV and V at 500 m distance from the asphalt plants. Asphalt is a residue from petroleum refining process which is known to contain substantial amounts of Ni. Similar levels of Ni were reported in surface soils of industrial zones in south-western Nigeria (Umoren and Onianwa, 2005). The concentrations of Ni observed in these sites were higher than the concentrations of Ni found in soils in the vicinity of gas plant (Iwegbue et. al., 2006) and crude oil contaminated sites in the Niger Delta (Iwegbue et. al., 2009).

The concentrations of Cr in these soil profiles ranged from 9.0 - 189 mg kg^{-1} within the plants and from 37.0-107 mg kg^{-1} at 500 m distance from the plants. Higher concentrations of Cr were found in the soil profiles of sites IV and V compared to the other sites investigated. The Department of Petroleum Resources maximum allowable level of Cr in soil is 100 mg kg^{-1}. The concentrations of Cr in the top and sub soil samples collected within the asphalt plants were above the maximum allowable levels of Cr in soil, while at 500 m distance, only the topsoil of site V had higher concentration of Cr than the limit. Inuwa et. al. (2007) reported Cr concentration in the range of 21.1-85.4 mg kg^{-1} in surface soil around industrial areas in the northern part of Nigeria. The concentrations of Cr observed in these soils were higher than the concentrations of Cr in soils around some industries in Nigeria (Inuwa et. al., 2007; Iwegbue et. al., 2007) but were comparable to the concentrations of Cr in soils of urban industrial zones in south western Nigeria (Umoren and Onianwa, 2005).

The concentrations of Cu in these soil profiles ranged from 2.0-31.0 mg kg^{-1} within the asphalt plants and from 1.9-28.0 mg kg^{-1} at 500 m distance from the asphalt plants. Lower concentrations of copper were observed in the subsoil compared to the concentrations of Cu observed in the topsoil. The concentrations of Cu found in these sites were lower than the Department of Petroleum Resources of Nigeria permissible limit of 36 mg kg^{-1} Cu in soil. The concentrations of Cu found in these sites were lower than the DPR target value. The concentrations of Cu we found in our sites were higher than concentrations of Cu observed in soils in the vicinity of crude oil processing facilities in Nigeria (Iwegbue et. al., 2006; Iwegbue et. al., 2009). Much higher Cu levels (68.8 to 103.3 mg kg^{-1}) were reported in soils in the vicinity of cement factory in Nigeria (Maina et. al., 2009) and in soils near copper smelter in Poland (Kabala and Singh, 2001). Copper is complexed by organic ligands especially by the carboxylic and phenolic groups. As the solubility of the organic matter increases with increasing pH, the dissociation of Cu – organic matter complexes can result in the leaching of copper to ground water (Bhattacharya et. al., 2002). The solubility of Cu and Zn is governed by pH and redox conditions and at pH range of 5.4-6.5, Cu and Zn are distinctly more soluble under oxidising conditions than reducing conditions (Bhattacharya et. al., 2002). In the present study, only the subsoil of site III had pH value in this range, the solubility of Cu and Zn is unlikely in these sites.

The concentrations of Co in these soil profiles were in the range of 2.0 to 11.1 mg kg^{-1}. The highest concentrations of Co were observed in the soil profile of site II (Table 4). Like other metals, the concentrations of Co were higher in the soil samples collected within the asphalt plants than those collected at 500 m distance from the plants. The Department of Petroleum Resources of Nigeria permissible limit of Co in soil is 20 mg kg^{-1} (DPR, 2002). The concentrations of Co, found in our sites, were below the specified limit of Co in soil by the Nigerian regulation. The concentrations of Co observed in these sites were lower than concentrations of Co in soils around industrial sites in southern India (Krishna and Govil, 2008). However, Co concentrations in the range of 3.55 to 58.9 mg kg^{-1} have been reported in urban soils of different cities in China (Zhang and Ke, 2004; Lu and Bai, 2006; Lee et. al., 2006; Liao et. al., 2006; Luo et. al., 2012b).

The concentrations of Fe in these soil profiles ranged from 58.0 to 247 mg kg^{-1}. The highest concentration of Fe was observed in the soil profile of site II. The concentrations of Fe observed in these soil profiles were below global average value (Alloway, 2005) and crustal abundance value of Fe of 47000 mg kg^{-1}. The concentrations of Fe in these soils samples were lower than the concentrations of Fe previously reported for the Niger Delta soils (Iwegbue et. al., 2006; Nwajei and Iwegbue, 2010; Iwegbue et. al., 2009a; Iwegbue, 2013).

The concentrations of Mn in these soil samples ranged between 54.1 and 278 mg kg^{-1} for all sites and depths. The highest concentration of Mn was observed in the topsoil of site II. The distribution patterns of Mn in the topsoil of these sites follow the order II > V > I > III > IV. The concentrations of Mn found in these soil profiles were below the crustal abundance and global average values (Alloway, 2005; Turiekian and Wedepohl, 1961). The concentrations of manganese were about 1.13 to 1.84 times higher than levels observed at 500m distance from the asphalt plants. However, the concentrations of Mn in the soil profiles of these asphalt plants were comparable to the concentrations of Mn observed in soils in the vicinity of gas plant (Iwegbue et. al., 2006) and crude oil impacted soils (Iwegbue et. al., 2009b) but were lower than the concentrations of Mn found in soils around

a cement industry in Nigeria (Maina et. al., 2009). The concentration of Mn in soils is of significance because of its high mobility. It migrates easily and contaminates surface streams and ground water.

The concentrations of Zn in all sites and depths varied from 32.0-102 mg kg^{-1} within the asphalt plants and from 21.2 to 92.9 mg kg^{-1} at 500 m distance from the asphalt plants. The higher concentrations of Zn were observed in sites I and III than other sites investigated. The Department of Petroleum Resources of Nigeria permissible limit for Zn in soil is 140 mg kg^{-1} (DPR, 2002). The concentrations of Zn observed in soils collected from all sites and depths were below the DPR limit. Similar Zn concentrations have been reported in soils in the vicinity of industrial activities in Nigeria (Iwegbue et. al., 2006; Iwegbue et. al., 2009; Maina et. al., 2009) and other regions of the world (Kabala and Singh, 2001).

3.1. Contamination/Pollution Index

As shown in Table 5, the index values for Cd, Cu, Fe, Mn and Zn were in the contamination range (i.e., less than unity), whereas that of Cr and Ni were in the pollution range (i.e., greater than unity). The multiple pollution index value for these sites ranged from 1.6 to 5.5 with a significant contribution from Ni and Cr. The MPI values decreased with increasing depths of the profiles, which indicated that the surface soils were more polluted than the subsurface soils. Again, the MPI values can be used to rank the various sites and depths in order of magnitude of pollution. In this case, the magnitudes of pollution by these metals followed the order: II > V > IV > III > I.

Table 5: Contamination/Pollution index for soils within the plants and 500 m from the Asphalt plant

Within the asphalt plant									
Site	**Depth (cm)**	**Cd**	**Pb**	**Ni**	**Cr**	**Cu**	**Co**	**Zn**	**MPI**
I	0-15	0.4	0.0	3.2	1.6	0.8	0.4	0.7	4.7
	15-30	0.2	0.0	2.4	0.1	0.3	0.2	0.5	2.4
	30-60	0.1	0.0	1.8	0.1	0.3	0.1	0.4	2.3
II	0-15	0.5	0.1	3.3	1.5	0.9	0.5	0.2	4.8
	15-30	0.4	0.0	3.0	1.9	0.3	0.1	0.6	4.9
	30-60	0.2	0.0	2.5	0.1	0.3	0.2	0.4	2.5
III	0-15	0.4	0.0	3.6	1.7	0.7	0.5	0.7	5.2
	15-30	0.2	0.0	2.9	1.5	0.6	0.4	0.6	4.4
	30-60	0.1	0.0	1.6	0.0	0.3	0.1	0.4	1.6
IV	0-15	0.4	0.0	4.0	1.8	0.3	0.6	0.4	2.6
	15-30	0.1	0.0	3.3	1.5	0.2	0.3	0.3	4.8
	30-60	0.1	0.0	2.7	1.2	0.1	0.2	0.2	3.9
V	0-15	0.4	0.0	3.9	1.7	0.3	0.5	0.4	5.5
	15-30	0.3	0.0	3.1	1.5	0.2	0.2	0.3	4.6
	30-60	0.1	0.0	2.6	1.3	0.1	0.1	0.3	3.9
500 m distance from the asphalt plant									
I	0-15	0.2	0.0	1.9	1.0	0.5	0.3	0.7	1.9
	15-30	0.2	0.0	1.2	0.6	0.2	0.2	0.4	1.2
	30-60	0.1	0.0	1.1	0.5	0.1	0.1	0.4	1.1
II	0-15	0.2	0.0	3.7	0.9	0.8	0.3	0.6	3.7
	15-30	0.2	0.0	3.6	0.6	0.4	0.2	0.4	3.6
	30-60	0.1	0.0	3.0	0.5	0.3	0.1	0.4	3.0
III	0-15	0.2	0.0	1.1	1.1	0.3	0.4	0.3	2.2
	15-30	0.1	0.0	2.1	0.6	0.3	0.2	0.4	2.1
	30-60	0.1	0.0	3.0	0.5	0.3	0.1	0.4	3.0
IV	0-15	0.2	0.0	2.2	0.9	0.2	0.2	0.3	2.2
	15-30	0.1	0.0	1.1	0.6	0.1	0.1	0.2	1.1
	30-60	0.1	0.0	0.6	0.4	0.1	0.1	0.2	0.0
V	0-15	0.2	0.0	2.0	1.0	0.3	0.4	0.3	2.0
	15-30	0.2	0.0	2.1	0.9	0.2	0.3	0.3	2.1
	30-60	0.9	0.0	0.6	0.4	0.1	0.1	0.0	0.6

3.2. Enrichment factor and Geoaccumulation index

The estimated Enrichment Factors (EF) for metals in soils within the asphalt plants and at 500 m distance from the plant are displayed in Table 6. Apart from Cd, Cr and Ni other metals had EF values less than 1. The enrichment factors decreased in the order; Ni > Cr > Cd > Cu > Co > Pb > Mn > Fe. In the present study, the soil collected within the asphalt plants had higher EF values than those collected at 500 m distance from the asphalt plants. EF values for the metals in these soils decreased with depth and lateral distance from the plant which indicated that surface horizons of these sites were more enriched with metals than subsurface horizon and moreso, soils within the plants were enriched with metals than those collected at a distance away from the plant. From contamination categorisation based on the enrichment factor values, the soils within and at a distance from the asphalt plants fall within the deficiency to minimal enrichment to moderate enrichment categories.

The geoaccumulation index (Igeo) for the examined metals in these soils are displayed in Table 7. The Igeo values of the examined metals for all sites, depths and 500 m distance from the asphalt plants were negative which also indicated that these sites were not polluted with the studied metals. Igeo values observed in these sites, depths and distance from the plants indicate that the examined soils fall within the class 1 (no pollution) of the Igeo categorization.

Table 6: Enrichment factor of soils within the plants and 500 m distance from the asphalt plants

		Within the asphalt plant					500 m distance from the asphalt plant				
Metals	**Depth (cm)**	**I**	**II**	**III**	**IV**	**V**	**I**	**II**	**III**	**IV**	**V**
Cd	0-15	1.07	1.27	1.07	0.97	1.03	0.57	0.50	0.43	0.50	0.47
	15-30	0.50	0.93	0.47	0.33	0.67	0.40	0.43	0.37	0.37	0.43
	30-60	0.37	0.47	0.37	0.23	0.37	0.33	0.37	0.33	0.27	0.23
Pb	0-15	0.17	0.20	0.15	0.15	0.15	0.10	0.14	0.09	0.08	0.07
	15-30	0.05	0.10	0.11	0.07	0.08	0.06	0.05	0.05	0.05	0.08
	30-60	0.04	0.06	0.05	0.05	0.05	0.05	0.04	0.04	0.04	0.03
Ni	0-15	1.69	1.75	1.88	2.10	2.03	0.96	1.93	1.41	1.13	1.03
	15-30	1.29	1.58	1.56	1.76	1.66	0.62	1.86	1.06	0.55	1.10
	30-60	0.93	1.34	0.87	1.43	1.38	0.56	1.52	1.55	0.31	0.30
Cr	0-15	1.73	1.66	1.83	1.95	1.85	1.08	0.98	1.19	1.00	1.13
	15-30	0.14	2.10	1.63	1.66	1.66	0.68	0.67	0.62	0.63	0.97
	30-60	0.10	0.13	0.10	1.35	1.40	0.56	0.55	0.56	0.41	0.46
Cu	0-15	0.64	0.69	0.58	0.23	0.27	0.42	0.62	0.20	0.13	0.27
	15-30	0.28	0.24	0.47	0.14	0.18	0.16	0.27	0.25	0.09	0.13
	30-60	0.22	0.20	0.23	0.04	0.10	0.09	0.22	0.22	0.04	0.04
Co	0-15	0.43	0.50	0.50	0.55	0.49	0.32	0.33	0.37	0.34	0.35
	15-30	0.21	0.49	0.43	0.31	0.09	0.20	0.21	0.15	0.21	0.30
	30-60	0.11	0.20	0.10	0.20	0.10	0.10	0.10	0.10	0.11	0.10
Fe	0-15	0.01	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
	15-30	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	30-60	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mn	0-15	0.22	0.33	0.19	0.18	0.23	0.19	0.18	0.09	0.08	0.11
	15-30	0.08	0.09	0.09	0.08	0.10	0.10	0.07	0.08	0.07	0.07
	30-60	0.07	0.07	0.07	0.06	0.07	0.06	0.05	0.05	0.06	0.06
Zn	0-15	1.07	0.34	1.05	0.53	0.64	0.98	0.95	0.49	0.43	0.44
	15-30	0.69	0.85	0.84	0.45	0.44	0.60	0.64	0.59	0.28	0.42
	30-60	0.55	0.63	0.62	0.34	0.38	0.51	0.52	0.53	0.22	0.01

3.3. Principal Component Analysis

The PCA factor loading after Varimax rotation with Kaiser Normalization of metals in the soil profiles within the asphalt plants and at 500 m distance from the plants are displayed in Tables 8 and 9, respectively. PCA factor loading for soils within the asphalt plants have been previously described (Iwegbue, 2013). Briefly, two factors were obtained accounted for 91.33% of the total variance at 0-15 cm depth of the immediate vicinity of the plant. Factor 1 accounted for 59.07% of the total variance and was dominated by total organic carbon, Cd, Fe, Cu, and Pb. This suggests that the mechanism for the retentions of these metals in the topsoil is due to complexation to organic matter (Romic et. al., 2004). Copper has a higher loading of 0.993 than the other metals, which might be explained by the chalcophilic characters of these elements (they form sulphide which is poorly soluble minerals, e.g., Cu_2S, CuS and CdS etc). In contrast to Cd, most colloidal particles in soil strongly adsorb Cu. Copper

forms a stable complex with organic matter than other bivalent transition metals and, therefore, soil, which is rich in organic matter, can retain more copper without causing plant toxicity. Bipolarity of factor with a higher negative loading for Cr and Ni and somewhat lower loading for Mn and Co were observed. Factor 2 explained 32.26% of the total variance with significant loading in Mn, Zn, pH and conductivity. Again, the retention of these metals (Mn and Zn) in the soil is pH dependent. Mn and Zn are associated with traffic activities. Zn may be derived from mechanical abrasion of vehicles. Zinc in these soils may therefore be related, in part, to traffic movement within these sites. Zinc compounds have been employed extensively as antioxidants, e.g., (zinc carboxylate complexes and zinc sulphonates) and as detergent dispersant improvers for lubricating oil (Miguel et. al., 1997). It was reported that tire wear contributes significant amounts of Zn to the environment. However, Mn is a fuel additive, especially in diesel which is used to run the plants and truck used haulage of the processed asphalt. At the 15-30 cm depth, the PCA results showed that 3 principal components were extracted, accounting for 46.13%, 30.98% and 19.53% of the total variance. Factor 1had a significant positive loading in Cu, Mn, Zn, Cd, Pb and conductivity. Chemisorption on the Mn and Al oxides may explain this association. Factor 2 had a significant loading in Fe, Cd, Zn and organic matter while factor 3 had significant loading in Cr and conductivity. The bipolarity factor of the second factor with a high negative factor loading for Ni and somewhat lower loading for Co, Cr, Pb and Cu, was observed as well (Table 8). At the 30-60 cm depth, the PCA results indicated that three components were extracted. Factor 1 had a significant positive loading for Zn, Cu, Cd and Ni consisting of 78.38% of total variance. The bipolarity of the first factor with high negative factor loading for Fe and Mn and a negative loading for TOC and electrical conductivity. Factor 2 accounted for 13.95% of the total variance with the dominance of metal such as Pb, Cr, Co and electrical conductivity, and a high negative bipolar factor in Zn, Mn, Cu and pH and TOC. Factor 3 constitutes 8.55% the total variance comprising Pb, Cd, Cr, Co and with high negative bipolar factor in pH and TOC.

Table 7: Geoaccumulation index for soils within the plants and 500 m distance from the asphalt plants

		Within the asphalt plant					500 m distance from the asphalt plant				
Metals	**Depth (cm)**	**I**	**II**	**III**	**IV**	**V**	**I**	**II**	**III**	**IV**	**V**
Cd	0-15	-0.49	-0.24	-0.49	-0.63	-0.54	-1.40	-1.59	-1.79	-1.59	-1.68
	15-30	-1.59	-0.68	-1.68	-2.17	-1.17	-1.91	-1.79	-2.03	-2.03	-1.79
	30-60	-2.03	-1.68	-2.03	-2.68	-2.03	-2.17	-2.03	-2.17	-2.49	-2.68
Pb	0-15	-3.11	-2.88	-3.32	-3.29	-3.33	-3.89	-3.45	-4.13	-4.31	-4.46
	15-30	-4.88	-3.92	-3.83	-4.34	-4.27	-4.61	-4.88	-4.92	-4.94	-4.22
	30-60	-5.12	-4.73	-4.97	-4.86	-4.86	-4.97	-5.14	-5.12	-5.40	-5.57
Ni	0-15	0.17	0.22	0.33	0.49	0.44	-0.65	0.36	-0.09	-0.41	-0.55
	15-30	-0.21	0.07	0.05	0.23	0.15	-1.28	0.31	-0.50	-1.45	-0.45
	30-60	-0.70	-0.16	-0.79	-0.06	-0.12	-1.43	0.02	0.04	-2.27	-2.34
Cr	0-15	0.21	0.15	0.29	0.38	0.30	-0.48	-0.61	-0.33	-0.59	-0.40
	15-30	-3.45	0.49	0.12	0.14	0.15	-1.14	-1.17	-1.28	-1.26	-0.62
	30-60	-3.91	-3.49	-3.90	-0.16	-0.10	-1.43	-1.45	-1.43	-1.86	-1.70
Cu	0-15	-1.23	-1.12	-1.37	-2.74	-2.46	-1.82	-1.26	-2.91	-3.49	-2.49
	15-30	-2.44	-2.66	-1.68	-3.44	-3.08	-3.21	-2.45	-2.61	-4.03	-3.56
	30-60	-2.79	-2.91	-2.69	-5.08	-3.85	-3.99	-2.77	-2.76	-5.09	-5.18
Co	0-15	-1.80	-1.58	-1.58	-1.44	-1.62	-2.24	-2.19	-2.01	-2.14	-2.09
	15-30	-2.83	-1.62	-1.80	-2.29	-4.10	-2.91	-2.87	-3.29	-2.87	-2.33
	30-60	-3.78	-2.91	-3.91	-2.90	-3.92	-3.91	-3.88	-3.91	-3.80	-3.93
Fe	0-15	-8.10	-8.10	-8.25	-8.30	-8.18	-8.55	-9.16	-9.09	-8.70	-8.87
	15-30	-9.49	-9.44	-9.29	-9.35	-9.25	-9.62	-10.03	-9.60	-9.67	-9.63
	30-60	-9.81	-9.68	-9.75	-9.82	-9.76	-10.02	-10.22	-10.25	-10.13	-9.95
Mn	0-15	-2.80	-2.20	-2.95	-3.08	-2.71	-2.98	-3.07	-4.11	-4.18	-3.80
	15-30	-4.15	-4.11	-4.06	-4.19	-3.91	-3.87	-4.50	-4.19	-4.35	-4.33
	30-60	-4.51	-4.38	-4.39	-4.56	-4.38	-4.76	-4.89	-4.91	-4.73	-4.54
Zn	0-15	-0.49	-2.16	-0.51	-1.51	-1.23	-0.62	-0.67	-1.60	-1.79	-1.76
	15-30	-1.13	-0.82	-0.84	-1.73	-1.79	-1.33	-1.22	-1.34	-2.40	-1.84
	30-60	-1.45	-1.25	-1.27	-2.15	-1.98	-1.55	-1.52	-1.51	-2.75	-7.17

  - Volume 7, (Number 1), (ISSN 1995-6681)

Table 8: PCA Factor loadings after varimax rotation with Kaiser Normalization for heavy metals in soil profile within asphalt plants

	0-15 cm		15-30 cm			30-60 cm		
Parameter	**Factor 1**	**Factor 2**	**Factor 1**	**Factor 2**	**Factor 3**	**Factor 1**	**Factor 2**	**Factor 3**
Fe	.871	.105	-.6.17E-02	.996	-2.91E-02	-.829	.002	.371
Mn	-.548	.784	.963	.227	8.79E-02	-.605	-.637	.458
Zn	-1.28E-03	.952	.979	.174	4.78E-02	.586	-.737	.337
Cu	.933	.177	.961	-.211	-4.38E-02	.790	-.556	-.018
Pb	.879	-.408	.914	-.302	-.190	-.083	.513	.843
Cd	.882	-.420	.610	.769	-.186	.639	.301	.529
Cr	-.984	1.318E-02	-.443	-.142	.885	.080	.681	.724
Co	-.577	-.734	-.715	-.575	.363	.036	.793	.518
Ni	-.943	-.314	.479	-.797	-.288	.999	.029	.013
pH	-.666	.683	-.117	-.8.23E-02	-.988	.152	-.214	-.933
Conductivity	.319	.938	.668	-.324	.669	-.218	.792	.562
TOC%	.920	6.97E-02	5.50E-02	.868	-.128	-.151	-.332	-.691
Var. (%)	**59.07**	**32.26**	**46.13**	**30.98**	**19.53**	**76.38**	**13.95**	**8.55**

At 500 m distance from the asphalt plants, only three components were extracted from the data set for the 0-15 cm depth (Table 9). Factor 1 expresses about 58.12% of the total variance which was dominated by Cd, Cr, Cu, Ni and Zn which had no association with the soil physicochemical characteristics. The PCA results indicate that these metals are of anthropogenic origin. Factor 2 expresses about 23.94% of total variance including Co, conductivity and TOC and factor 3 expresses 15.73% of the total variance with a significant loading in Fe and pH. Factors 2 and 3 explain the fact that the presence of Fe and Co in soils was purely of pedogenic and lithogenic origin. However, the retention mechanisms of these metals in these soils are entirely different. The association of Fe and pH suggested that Fe was retained in the exchange sites while organic complexation is the prevailing retention mechanism for Co in this depth. At the 15-30 cm depth, four principal components were extracted. Factor 1was dominated by Mn, Pb, Cr, Co, Ni which accounts for 44% of the total variance. Factor 2 was comprised of Zn, Cu, Pb, Cd, Co and conductivity, and accounted for 29.9 % of the total variance. Factor 3 consisted of Fe and conductivity and factor 4 was dominated by Ni, TOC and conductivity accounting for 9.33% of the total variance. At 30-60 cm depth three principal components were extracted accounting for 49.33%, 27.98% and 15.71% of the total variance. Factor 1 included Cu, Zn and organic matter. Complexation to organic matter explained the retention of Zn and Cu in the soil. Factor 2 comprised of Fe, Pb, Mn and somewhat low loading for Cd which indicated that Pb was associated Fe-Mn oxides and factor 3 was dominated by Co, Pb, Ni and pH, which indicated that these metals occurred at the exchangeable sites. Bipolarity of factor 1 showed high negative loading for Cr and Ni while the bipolarity of factor 3 showed a high negative loading for Cd.

Table 9: PCA Factor loadings after varimax rotation with Kaiser Normalization for heavy metals in soil profile at 500 m from asphalt plant

	0-15 cm			15-30 cm				30-60 cm		
Parameter	**Factor 1**	**Factor 2**	**Factor 3**	**Factor 1**	**Factor 2**	**Factor 3**	**Factor 4**	**Factor 1**	**Factor 2**	**Factor 3**
Fe	-.749	-.238	.617	.346	1.20E-02	.934	9.055E-02	.313	.817	.478
Mn	-.951	-9.53E-02	.283	.864	-3.61E-02	.495	8.292E-02	.193	.911	-2.23E-02
Zn	.984	-.112	5.941E-02	.184	.774	-.494	-.350	.934	.343	7.710E-02
Cu	.814	-.333	-.455	-8.22E-02	.961	.129	-.230	.955	.218	-.147
Pb	.872	-.201	.373	.830	.541	.126	-4.72E-02	-.355	.621	.664
Cd	.977	-.163	4.476E-02	.140	.920	.367	-4.15E-03	.414	.469	-.673
Cr	.754	-.648	.105	.980	-9.67E-02	.142	.139	-.994	-6.99E-02	-2.84E-02
Co	3.256E-02	.989	-.101	.763	.553	-.335	1.38E-02	-.218	-.113	.785
Ni	.778	-.322	-.516	.688	-.312	.379	.534	-.775	.125	.620
pH	9.199E-02	.255	.941	-6.70E-02	-.232	-.967	8.262E-02	.335	.134	.887
Conductivity	-.485	.832	.256	.450	.604	9.403E-02	.658	-.244	-.913	.299
TOC%	6.220E-02	.533	-.838	3.22E-02	-.314	-.3.46E-02	.948	.923	.271	-.175
Var. (%)	**58.12**	**23.94**	**15.73**	**44.00**	**29.94**	**17.64**	**9.33**	**49.33**	**27.98**	**15.71**

3.4. Ecological Risk Assessment

The ecological risk (RI) is a measure of the sensitivity of various biological communities to toxic substances and illustrates the potential ecological risk caused by metals (Benhaddya and Hadjel, 2014). The ecological risks of metals in the studied soil profiles are displayed on Table 10. The ecological risk index (RI) of metals in these soil profiles ranged from 13.0 to 58.0 with significant contributions from Cd, Ni and Cr. The highest ecological risk index value was obtained in the premises of site II. The ecological risk index of metals in these soil profiles were less than 150 which suggests low ecological risks.

Table 10: Ecological risk assessment of metals in soil in the vicinity of asphalt plants.

Sites	Depth (cm)	Cd	Pb	Ni	Cr	Cu	Co	Zn	RI
Within Plant									
I	0-15	30.0	0.88	8.46	3.47	3.20	0.91	1.07	48.0
	15-30	20.0	0.25	6.46	0.28	1.38	0.44	0.69	29.5
	30-60	10.0	0.23	4.63	0.20	1.08	0.23	0.55	16.9
II	0-15	40.0	1.03	8.76	3.33	3.46	1.06	0.34	58.0
	15-30	30.0	0.50	7.88	4.21	1.19	1.03	0.85	45.7
	30-60	10.0	0.28	6.71	0.27	1.00	0.42	0.63	19.3
III	0-15	30.0	0.75	9.42	3.67	2.90	1.06	1.05	48.9
	15-30	10.0	0.53	7.78	3.27	2.33	0.91	0.84	25.6
	30-60	10.0	0.25	4.35	0.20	1.16	0.21	0.62	16.8
IV	0-15	30.0	0.78	10.52	3.91	1.12	1.17	0.53	48.0
	15-30	10.0	0.38	8.82	3.32	0.69	0.65	0.45	24.3
	30-60	10.0	0.25	7.18	2.69	0.22	0.42	0.34	21.1
V	0-15	30.0	0.75	10.15	3.69	1.37	1.03	0.64	47.6
	15-30	20.0	0.40	8.32	3.33	0.89	0.19	0.43	33.6
	30-60	10.0	0.25	6.90	2.80	0.52	0.21	0.38	21.1
500 m away									
I	0-15	20.0	0.50	4.78	2.15	2.12	0.67	0.98	31.2
	15-30	10.0	0.30	3.10	1.36	0.81	0.42	0.60	16.6
	30-60	10.0	0.25	2.79	1.12	0.48	0.21	0.51	15.4
II	0-15	20.0	0.70	9.63	1.96	3.12	0.69	0.95	37.1
	15-30	10.0	0.25	9.29	1.34	1.38	0.43	0.64	23.3
	30-60	10.0	0.23	7.58	1.10	1.10	0.21	0.52	20.7
III	0-15	10.0	0.43	7.07	2.38	1.00	0.78	0.49	22.1
	15-30	10.0	0.25	5.30	1.24	1.23	0.33	0.59	18.9
	30-60	10.0	0.23	7.73	1.11	1.11	0.21	0.53	20.9
IV	0-15	20.0	0.38	5.65	2.00	0.67	0.72	0.43	29.8
	15-30	10.0	0.25	2.74	1.25	0.46	0.43	0.28	15.4
	30-60	10.0	0.18	1.55	0.82	0.22	0.23	0.22	13.2
V	0-15	10.0	0.35	5.13	2.27	1.33	0.74	0.44	20.3
	15-30	10.0	0.40	5.49	1.95	0.63	0.63	0.42	19.5
	30-60	10.0	0.15	1.48	0.93	0.21	0.21	0.01	13.0

3.5. Non-carcinogenic hazard and carcinogenic risks

The non-carcinogenic and carcinogenic risks, evaluated based on the total metal concentrations for the children and adult scenarios, are displayed in Tables 11 and 12, respectively. The non-carcinogenic hazards of the different exposure pathways indicated that HQing>>HQderm>>HQinh for the children-which is possible due to hand-to-mouth habits of children, whereas, in the case of adult, HQinh>>HQing>>HQderm. Cumulatively, the HI for the children scenario ranged from 0.17 to 1.37 and 0.28 to 0.86 within the asphalt plant and 500 m distance from the asphalt plants, respectively. The HI of

metal for adult's case ranged from 0.27 to 1.26 for all sites and depths. Although, the HI values were slightly greater than 1 in 53% of the samples for the children scenario and 33% of the samples for the adult scenario within the asphalt plants. The cumulative HI for exposure via the three major exposure pathways at 500 m distance from the asphalt plant were less than 1 for the adult and children scenarios. Overall, the non-carcinogenic risks of metals in soil were higher at the premises of the asphalt plants than at 500 m distance from the plants.

Table 11: Non-carcinogenic hazard exposure to metals in soil in the vicinity of asphalt plant.

		CHILD				ADULT			
Within Plant	**Depth(cm)**	HQ_{ing}	HQ_{inh}	HQ_{derm}	HI	HQ_{ing}	HQ_{inh}	HQ_{derm}	HI
I	0-15	1.03	0.0017	0.13	1.17	0.17	0.83	0.025	1.03
	15-30	0.28	0.0007	0.01	0.29	0.05	0.34	0.003	0.39
	30-60	0.17	0.0005	0.01	0.18	0.03	0.24	0.002	0.27
II	0-15	1.08	0.0021	0.13	1.21	0.18	1.05	0.024	1.26
	15-30	1.18	0.0013	0.16	1.34	0.20	0.65	0.030	0.87
	30-60	0.27	0.0006	0.01	0.28	0.04	0.32	0.003	0.36
III	0-15	1.13	0.0017	0.14	1.27	0.19	0.84	0.027	1.06
	15-30	0.97	0.0012	0.13	1.10	0.16	0.58	0.024	0.77
	30-60	0.16	0.0005	0.01	0.17	0.03	0.24	0.002	0.27
IV	0-15	1.21	0.0017	0.15	1.36	0.20	0.86	0.028	1.09
	15-30	0.89	0.0011	0.13	1.02	0.15	0.55	0.024	0.72
	30-60	0.68	0.0009	0.10	0.78	0.12	0.42	0.019	0.55
V	0-15	1.12	0.0019	0.14	1.27	0.19	0.91	0.027	1.13
	15-30	0.72	0.0010	0.13	0.85	0.12	0.50	0.024	0.64
	30-60	0.62	0.0008	0.11	0.73	0.11	0.40	0.020	0.53
500 m away									
I	0-15	0.68	0.0013	0.08	0.77	0.12	0.63	0.016	0.76
	15-30	0.43	0.0007	0.05	0.48	0.07	0.36	0.010	0.44
	30-60	0.30	0.0005	0.04	0.34	0.05	0.23	0.008	0.29
II	0-15	0.70	0.0014	0.08	0.78	0.12	0.67	0.015	0.81
	15-30	0.47	0.0008	0.05	0.53	0.08	0.40	0.010	0.49
	30-60	0.34	0.0006	0.05	0.38	0.06	0.30	0.008	0.36
III	0-15	0.76	0.0010	0.09	0.86	0.13	0.51	0.017	0.65
	15-30	0.39	0.0007	0.05	0.44	0.07	0.34	0.009	0.42
	30-60	0.34	0.0006	0.05	0.39	0.06	0.30	0.009	0.36
IV	0-15	0.66	0.0009	0.08	0.74	0.11	0.45	0.015	0.58
	15-30	0.40	0.0006	0.05	0.45	0.07	0.30	0.009	0.38
	30-60	0.25	0.0004	0.03	0.28	0.04	0.20	0.006	0.25
V	0-15	0.71	0.0010	0.09	0.80	0.12	0.50	0.016	0.64
	15-30	0.62	0.0008	0.08	0.70	0.10	0.41	0.014	0.53
	30-60	0.26	0.0004	0.04	0.29	0.04	0.22	0.007	0.27

Table 12: Carcinogenic risk associated with metal exposure in soils in the vicinity of the asphalt plants

		CHILD				ADULT			
	Depth(cm)	$RISK_{ing}$	$RISK_{inh}$	$RISK_{derm}$	TOTAL CANCER RISK	$RISK_{ing}$	$RISK_{inh}$	$RISK_{derm}$	TOTAL CANCER RISK
I	0-15	8.25E-03	1.57E-04	1.92E-04	8.60E-03	1.40E-03	7.70E-02	3.60E-05	7.84E-02
	15-30	1.62E-03	8.87E-05	1.50E-05	1.73E-03	2.75E-04	4.35E-02	2.90E-06	4.38E-02
	30-60	1.41E-03	6.64E-05	1.10E-05	1.49E-03	2.39E-04	3.28E-02	2.10E-06	3.30E-02
II	0-15	8.91E-03	1.71E-04	1.84E-04	9.27E-03	1.51E-03	8.37E-02	3.45E-05	8.53E-02
	15-30	7.00E-03	1.25E-04	2.33E-04	7.36E-03	1.19E-03	6.13E-02	4.37E-05	6.25E-02
	30-60	1.75E-03	9.32E-05	1.50E-05	1.86E-03	2.96E-04	4.57E-02	2.80E-06	4.60E-02
III	0-15	7.79E-03	1.59E-04	2.03E-04	8.15E-03	1.32E-03	7.79E-02	3.81E-05	7.93E-02
	15-30	6.17E-03	1.25E-04	1.81E-04	6.48E-03	1.04E-03	6.12E-02	3.39E-05	6.23E-02
	30-60	1.55E-03	6.54E-05	1.10E-05	1.63E-03	2.62E-04	3.21E-02	2.10E-06	3.23E-02
IV	0-15	8.17E-03	1.73E-04	2.16E-04	8.56E-03	1.38E-03	8.48E-02	4.06E-05	8.62E-02
	15-30	5.41E-03	1.26E-04	1.84E-04	5.72E-03	9.17E-04	6.17E-02	3.44E-05	6.26E-02
	30-60	4.10E-03	9.85E-05	1.49E-04	4.35E-03	6.95E-04	4.83E-02	2.79E-05	4.90E-02
V	0-15	7.81E-03	1.67E-04	2.04E-04	8.18E-03	1.32E-03	8.19E-02	3.83E-05	8.33E-02
	15-30	5.56E-03	1.22E-04	1.84E-04	5.87E-03	9.42E-04	5.98E-02	3.46E-05	6.08E-02
	30-60	4.22E-03	9.55E-05	1.55E-04	4.47E-03	7.14E-04	4.68E-02	2.91E-05	4.76E-02
500 m away									
I	0-15	4.89E-03	8.92E-05	1.19E-04	5.10E-03	8.28E-04	4.38E-02	2.23E-05	4.46E-02
	15-30	3.00E-03	5.61E-05	7.52E-05	3.13E-03	5.08E-04	2.75E-02	1.41E-05	2.80E-02
	30-60	2.49E-03	4.91E-05	6.18E-05	2.60E-03	4.21E-04	2.41E-02	1.16E-05	2.45E-02
II	0-15	5.77E-03	1.56E-04	1.09E-04	6.04E-03	9.77E-04	7.67E-02	2.04E-05	7.77E-02
	15-30	2.71E-03	1.21E-04	7.40E-05	2.91E-03	4.59E-04	5.92E-02	1.39E-05	5.97E-02
	30-60	2.34E-03	9.99E-05	6.09E-05	2.50E-03	3.95E-04	4.90E-02	1.14E-05	4.94E-02
III	0-15	4.72E-03	1.09E-04	1.32E-04	4.96E-03	7.99E-04	5.36E-02	2.47E-05	5.44E-02
	15-30	2.61E-03	7.67E-05	6.86E-05	2.76E-03	4.42E-04	3.76E-02	1.29E-05	3.81E-02
	30-60	2.35E-03	1.02E-04	6.17E-05	2.51E-03	3.98E-04	4.98E-02	1.16E-05	5.02E-02
IV	0-15	4.06E-03	9.00E-05	1.11E-04	4.26E-03	6.87E-04	4.41E-02	2.07E-05	4.48E-02
	15-30	2.62E-03	4.86E-05	6.93E-05	2.74E-03	4.44E-04	2.38E-02	1.30E-05	2.43E-02
	30-60	1.78E-03	3.00E-05	4.57E-05	1.86E-03	3.01E-04	1.47E-02	8.60E-06	1.50E-02
V	0-15	4.21E-03	8.27E-05	1.26E-04	4.41E-03	7.12E-04	4.06E-02	2.36E-05	4.13E-02
	15-30	4.14E-03	8.99E-05	1.08E-04	4.34E-03	7.01E-04	4.41E-02	2.02E-05	4.48E-02
	30-60	1.76E-03	2.75E-05	5.13E-05	1.83E-03	2.97E-04	1.35E-02	9.60E-06	1.38E-02

For the carcinogenic risk assessment, only Cd, Pb, Ni and Cr were used. As shown in Table 10, the total cancer risk for the children scenario ranged from 1.63×10^{-3} to 9.27×10^{-3} with significant impact from the ingestion pathway. In the case of adults, the total cancer risk from exposure to metals in these soil profiles ranged from 1.38×10^{-2} to 8.6×10^{-2} with the highest impact from the inhalation pathway. The cancer risks for different exposure routes follow the order $Risk_{ingestion} >> Risk_{dermal} >> Risk_{inhalation}$ for the children scenario and $Risk_{inhalation} >> Risk_{ingestion} >> Risk_{dermal}$ in the case of adults. The carcinogenic risks of metals due to exposure to these soils through ingestion, inhalation and dermal contact exceeded the target value of 10^{-6} which indicates serious cancer risks for persons working within the asphalt plant and those whose farms are located within 1 km distance from the plants.

4. Conclusions

The concentrations of Cr and Ni in the soil profiles exceeded the maximum allowed levels in soils as specified by the Department of Petroleum Resources of Nigeria. The multiple pollution indexes indicate that the examined sites fall with the "slight pollution" to "severe pollution" ranges with significant contributions from Cr and Ni. The present study indicates that asphalt plants are a possible source of elevated concentrations of metal species (particularly Cd, Ni and Cr) in these soil profiles. The total ecological risk (RI) values of metals in these soil profiles were <150, which suggested low ecological risks for these soils. However, the total cancer risk of metals in these soil profiles exceeded the target value of ($1/10^6$) one in a million population of the risk of developing cancer. If this trend is allowed to continue unabated, it is most likely that the local food web complexes in the vicinity of these plants might be at the highest risk of the induced metals contamination.

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