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Journal of Advanced Studies in Agricultural, Biological and Environmental Sciences (JABE)

A Peer Reviewed & Refereed, International Open Access Journal

www.jabe.in **Vol.2.Issue.1.2015, E-ISSN:2394-2606**

FRACTIONATION OF SELECTED TRACE METALS IN SOIL OF AN AUTO-MECHANIC VILLAGE IN EFFURUN, DELTA STATE, NIGERIA

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Article History

Received on:18-02-2015

Revised on:15-03-2014

Accepted on:28-03-2014

ABSTRACT

The impact of Auto-mechanic villages on the surrounding environment especially in areas where proper environmental disposal procedures for wastes are not adhered to can be devastating. Soil samples taken from the vicinity and areas surrounding the the Warri/Effurun, Nigeria auto-mechanic village were analyzed for soil pH and total metal (Cu, Pb, Ni and Cd). Trace metal were determined by flame atomic absorption spectrometry after appropriate sodium carbonate fussiun and digestion. Important results are, Cu (102±18 mgkg-1), Pb (68.5±9.9 mgkg-1), Ni (121±51 mgkg-1), Cd (35±10 mgkg-1), pH (6.40±0.58). The concentrations of the metal in some of the sites were found to exceed most of the guideline values used. The concentrations of Cd in all the sites exceeded all guideline values. Sequential extraction of metals showed that 58% of the concentration of Cd is in the non-residual geochemical phases which showed that Cd is an important pollutant in the study area and a high level of anthropogenic input of the metal. The use of contamination/pollution index to ascertain the pollution status also revealed that three of the trace metals (Cu, Ni and Cd) put the study area in the pollution category with respect to the three metals. The soil environment around the mechanic village can thus be said to be polluted with respect to the three metals (Cu, Ni and Cd).

Key words: Auto-mechanic village; wastes; sodium carbonate fussiun; guideline values; soil environment; sequential extraction; non-residual geochemical phases; Warri/Effurun Nigeria; anthropogenic input; contamination/pollution index.

Cite this article: **Dr Samuel Omorovie Akporido et al**., *"**FRACTIONATION OF SELECTED TRACE METALS IN SOIL OF AN AUTO-MECHANIC VILLAGE IN EFFURUN, DELTA STATE, NIGERIA**". Journal of Advanced Studies in Agricultural, Biological and Environmental Sciences, 2(1): 2015, 25-38*

INTRODUCTION

The use of automobiles such as cars, buses, trailers, lorries, motorcycles, etc, imposes certain loads in form of pollutants on the soil, water, sediment, air and biota of the environment. Among pollutants that can enter the environment are carbon monoxide, sulphur dioxide from the exhaust of automobiles into the air, hydrocarbons and heavy metals from used lubricating oils, petroleum products and crude oil spilled into soils and water. Heavy metals and hydrocarbons (especially PAH) falls into the groups of pollutants that are directly harmful to man and other higher animals. Polycyclic Aromatic hydrocarbons (PAH) have been implicated as human and animal carcinogen [1, 2]. Heavy metals have toxic effects on man and this toxicity is enhanced because metals can bio-accumulate in the tissues of humans, animals and fish with this factor making the concentrations that reaches man from the food chain to be very high. Catastrophic episodes of metal poisoning have in fact been recorded involving mercury, lead, cadmium and arsenic [3].. Effect of individual heavy metals on man and animals are well documented [3, 4]. Other general effect of heavy metals and other pollutants such as petroleum hydrocarbons if they are present in high quantity include depletion of potable water, depletion of arable land, damage and loss of biodiversity [5 – 10] Industrialization and Urbanization are two important sources of heavy metals in the environment [3, 11 – 15] Sources of heavy metals are also well documented by Forstner and Whitman [3] and Nriagu and Porcyna [16]

The quantification of heavy metals and other pollutants in water, soil, sediment and biota and metal speciation in soils of the Niger Delta have also been undertaken extensively [17 – 31].

An Auto-mechanic village is where repair of various types of auto-mobiles are carried out. It consist of many automobile repair workshops The contribution of an Auto-mechanic village to environmental load of pollutants (especially heavy metals) is derived mainly from the spilling and dumping of used lubricating oils, fuel (gasoline and diesel), used motor batteries and metal scraps. The Warri/Effurun Auto-mechanic village which is actually located in Effurun town (Warri and Effurun are twin towns) has a high volume of activities and method of disposal of waste as at the time of this research work cannot be rated to conform to standard environmental protection safety measures. The soil land use in this area includes agriculture (crop farming) and commerce. The few crops grown in the area includes Yam (*Dioscorea sp*.), Tomatoes (*Solanum lycoperscium*), cassava (*Manihot esculanta*),maize (*Zea mays*) and fluted pumpkin (*Telfera occidentals).* Swamps are also found in the area with very small streams from which fishing also takes place. The need for regular environmental auditing of the area cannot be overstressed. The hypotensis to be tested here is that area where there is indiscriminate dumping of waste material such as used lubricating oil, petroleum products should have enhanced concentration of heavy metals in soil, water and other matrices in the area. The study examined the effect of dumping of waste such as used lubricating oil and petroleum product (e.g. gasoline anddiesel) on the soil in the area by determining the concentration of four trace heavy metals (Cd, Ni, Pb and Cu) and pH of the soil in the area.

Speciation studies of the heavy metals were also undertaken by sequential extraction of metals from the soil to determine mainly the extent of anthropogenic input of these metals into the environment.

MATERIALS AND METHOD

Description of Study Area:

The Warri/Effurun Auto-Mechanic village consist of many Auto-mechanic workshops and is located to the northwest of Warri and Effurun twin towns on the road from Warri to Sapele (Fig. I: Map of Study Area showing the mechanic village and the sampling sites).

Design of Study and Collection/Preservation of Samples

Samples were collected from five points separated by 500 m successively from each other starting from the mechanic village itself, outwards. Soil samples were collected twice in every season (i.e. once in each quarter of the year) for three years (three dry and three rainy seasons respectively) from November 2003 to July 2006. The sampling design consisted of delimiting in every sampling station a sampling area of 30m x 30m. This sampling area was then divided into 100 grid plots of 3m x 3m area. Thus thirty three grid plots were randomly selected from these plots, three replicates of pre-determined quadrates were established, and soil samples were taken from each. Samples were manually taken at 0 – 15 cm (surface) and 15 – 30 cm (subsurface). Grab samples collected at the surface and subsurface separately from the thirty three grid plots were mixed together in well labelled polyethylene bags to obtain one surface and one subsurface composite sample respectively. The method for extracting the soil from the surface and subsurface depths involve digging to the required depth and exposing a flat, vertical surface from which the samples were withdrawn using a plastic shovel. The soil samples were immediately taken to the laboratory where they were oven-dried at 80 ^{0}C for 2 hrs. Soil samples were collected for pH and the trace heavy metals (copper, Lead, Nickel, and Cadmium).

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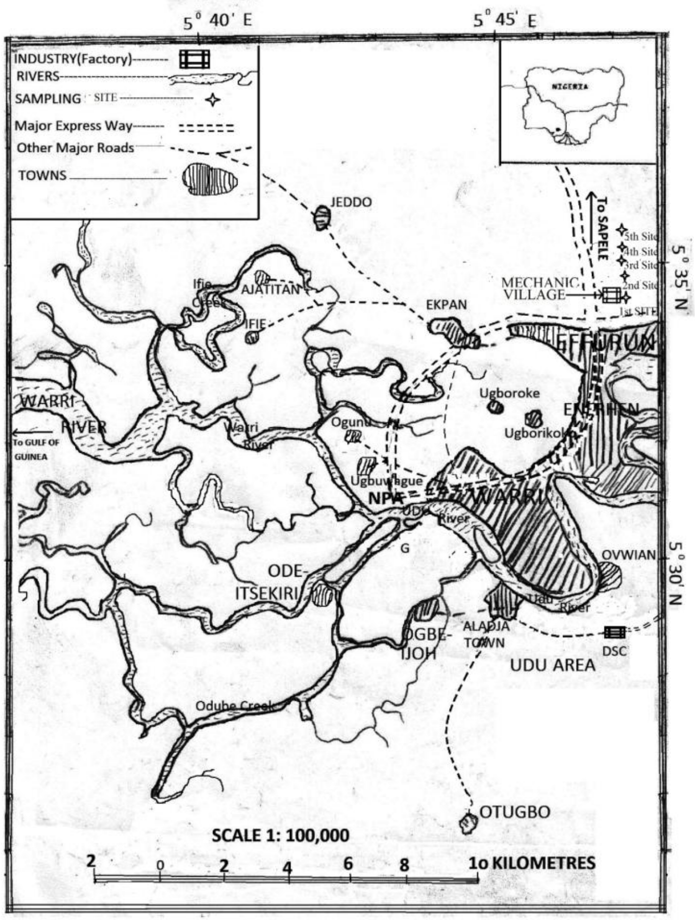

Fig. 1: map of study showing the Mechanic Village and the Sampling sites

Analytical Procedures

The parameters analyzed for are pH, copper, Lead, Nickel and Cadmium.

pH of Soil: This was carried out according to procedure by Folsom *et al,* [32], 5 g of oven-dried soil was weighed into a 100 ml beaker and 10 ml of distilled water was added and stirred to mix properly and allowed to stand for 5 mins. The pH meter electrode was dipped below the supernatant liquid above the settled soil.

Heavy Metals: Digestion of soil was done by the method of sodium carbonate fussion as describe in manual by Allens [33]. The concentration of metal in digest was determined by flame atomic absorption spectrophotometric method. The digest solution from the carbonate fussiun was filtered and subsequently analyzed using atomic absorption spectrophotometer (Perkin Elmer AA200) [33]. The Spetrophotometer was earlier calibrated with standard solutions of the four trace metals. A quality assurance programme was also put in place which involved analysis of blanks and duplicates. and determination of % recovery of the four metals. Average percentage recoveries of five determinations of each metal are, Cu (91.7±7.7 %), Pb (92.5±5.6 %), Ni (98±3.7 %), and Cd (94.6±6.5 %). This shows that the method for the determination of the metals in this study is a good one.

Sequential extraction of metals from soil: this was carried out with the method by Tessier and Campbell [34] in which five geochemical phases of metals i.e. Exchangeable, carbonate-bound Ferrous-manganese-bound; organic matter-bound and residual were extracted with appropriate reagents.

Calculation of contamination/pollution index:

The contamination/pollution (C/P) index for each metal in each sampling station was also calculated based on the mean value of each metal in each station for four seasons using the equation:

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$$\frac{C}{P}\,Index = \frac{Concentration\,of\,metal}{Tolerable\,level\,of\,metal\,in\,sediment}$$

The tolerable level of metal in sediment was taken to be the target value of the metal in the Environmental Guidelines and Standards for the petroleum industry in Nigeria (EGASPIN) [35].

$$\frac{C}{P}\,Index = \frac{Concentration\,of\,metal}{Target\,value\,of\,metal\,in\,sediment}$$

The results are given in Table 7 . The pollution (or contamination) status of the metals in the sampling stations are given the significance of interval of C/p Index in Table 8 [36].

The mobility factor which is an index of the bioavailability of trace metal ions can be calculated as follows [37]:

$$\text{Mobility factor} = \frac{F1+F2}{F1+F2+F3+F4+F5}\,x\,100$$

Where:

F1 = Exchangeable fraction

F2 = Carbonate bound fraction

F3 = Ferrous-manganese bound fraction

F4 = Organic matter bound Fraction

F5 = Residual fraction

Statistical packages and procedures employed:

The means of the concentrations of four trace heavy metal and pH in the six seasons were compared using analysis of variance (ANOVA – single factor) from Microsoft excel (2007 version). The means of the concentrations of the four trace heavy metals in the five sites were also compared using analysis of variance (ANOVA- single factor) from Microsoft excel (2007 version). The means of the concentrations of the four trace heavy metals and pH in the study are were also compared with the means of the corresponding parameters in the control area using t-test (two sample, assuming equal variances) from Microsoft excel (2007 version). The Pearson 2-tailed test was used for the correlation of the values of four trace heavy metals within the Statistic Package for the Social Sciences (SPSS) (version 17) (SPSS, Chicago).

RESULTS AND DISCUSSION

A comparison of the means of the levels of the four trace metals in the study area with the means of the corresponding parameter in the control area using a t-test (two sample, assuming equal variances) showed that there is a significant difference between the average concentration of the four metals in the study area soil and the control area soil (Table 1). A comparison of the average concentration of metals in the five sites (Table 1) using analysis of variance showed that there is no significant difference in the concentration of the four metals in the five sites (ANOVA-single factor). A comparison of the concentration of the four metals in the six seasons (Table 2) using Analysis of variance using (ANOVA-single factor) also showed that there is no significant difference in the six seasons.

Table 3 gives a comparison of the average concentration of the four metals and pH in each site with the Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health for different land uses (Agricultural, Residential/parkland, commercial and Industrial Land uses) [38]. It showed that the average concentration of copper in the five sites exceeded guideline values for Agricultural and Residential/parkland Land Uses. While average values of Cu for Sites II to Site far exceeded all guideline values for all land uses. Average values of lead in site II (70.1±8.9 mg/kg), site III (70.6±12 mg/kg) and site IV (75.0±7.2 mg/kg) exceeded guideline values for Agricultural land use (70 mg/kg). Average value of Ni in site I (154 ± 20 mg/kg), site III (158 ± 7.1 mg/kg) and site IV (159 ± 7.5 mg/kg) exceeded guideline values for all the land uses i.e. Agricultural (50 mg/kg). Residential/Parkland (50 mg/kg). Commercial (50 mg/kg) and industrial (50 mg/kg) land uses. The average concentration of Cd in all the sites I (35 ± 12 mg/kg), II (22.6 ± 5.9 mg/kg), III (31.6 ± 3.9 mg/kg), IV (43.2 ± 7.6 mg/kg) and V (41.1 ± 4.0 mg/kg) exceeded guideline values for all four land uses i.e. Agricultural (1.4 mg/kg), Residential/Parkland (10 mg/kg), Commercial (22 mg/kg) and Industrial (22 mg/kg) land uses. It appears that the soil of the study area is highly polluted with these trace metals. Comparing the average concentrations of the metals with soil guideline values (SGVs) for land uses is the best way to assess the pollution effect of each trace metal. According to Environment Agency [39] Soil guideline values (SGV) are 'trigger values' for screening – out low risk area of land contamination and they give an indication of representative average levels of chemicals in soil below which long-term health risk are likely to be minimal [39]. Although the study area showed high concentrations of these trace metals, it cannot be immediately concluded that the area is polluted to the extent of remediation being necessary. Speciation studies were carried out so as to know the propotion of each total metal in the non-residual a(bio-available) geochemical phases. This will enable conclusion to be drawn on the vulnerability of the area to human health risk associated with these trace metals. Average value of pH for Site II (5.89 $\pm$ 0.41 mg/kg) is lower than the pH range for all land uses (6 to 8).

Table 4 gives a comparison of average concentration of each metal in the study area with three other soil quality guidelines of other countries i.e. for Norway. Netherland (action level) and Switzerland and two soil quality guideline in use in Nigeria, they are guideline value for SPDC Ltd. (Shell Petroleum Development Company Limited) EIA (Environmental impact Assessment) process guidelines [40] and EGASPIN (Environmental guidelines and Standards for the Petroleum Industry in Nigeria) [35]. The average value of Cd for all five sites exceeded guideline values of Norway (1.00 mg/kg), Netherland (action level) (12.0 mg/kg), Switzerland guide value (0.8 mg/kg), SPDC Ltd EIA process guideline (0.70 – 3.00 $mgkg^{-1}$), EGASPIN Target value (0.80 $mgkg^{-1}$), EGASPIN Intervention value (12.0 $mgkg^{-1}$). The fact that the average values of Cd in the five sites exceeded the Intervention values of EGASPIN shows the seriousness of Cd pollution in the study area. EGASPIN Intervention values "indicate the quality for which the functionality of soil for human, animal and plant life are, or threatened with being seriously impaired. Concentrations in excess of the intervention values correspond to serious contamination" [35]. The average concentrations of the remaining three metals in some of sites studied also exceeded corresponding metal guideline values of the five other guidelines. This comparisons has also confirmed that there are elevated concentrations of the four trace heavy metals in the study area.

Results of sequential extraction experiment (speciation studies) of the metals in the soil of study area are given in Table 5. The results are given for each metal as follows:

Copper: The bio-available (non-residual) fraction constitutes 33.5 % of the total concentration of copper. The order of the concentrations in the five fractions is: Residual fraction > organic matter-bound > Fe – Mn oxide – bound > carbonate – bound >exchangeable. This order is to some extent in agreement with the order observed by most workers in which copper is known to be associated mainly with the organic matter-bound geochemical phase [41 – 44], the only difference is that in this case the residual fraction has the largest concentration. A greater proportion of the non-residual portion of the metal is in the organic matter-bound fraction.

Lead: The bio-available (non-residual) fraction constitute 38.9 % f the total concentration of lead. The order of concentration in the five fraction is, Residual > Fe-M oxide – bound = organic mattrr – bound > exchangeable > carbonate – bound. This also is to some extent in agreement with the order obtained by some workers [42, 45, 46] in which they found that Pb has its largest concentration in the Fe-Mn oxide – bound fraction where lead in acid soil and sediment is known to be adsorbed to amorphous and crystalline Fe oxide. The slight difference is that here most of the metal is in the residual geochemical phase. Another difference is that the organic matter-bound fraction has equal amount of the metal in the non-residual phase with the Fe-Mn oxide – bound fraction.

Nickel: Ni has 41 % of its total concentration in the non-residual (bio-available) geochemical phases. The order of the concentrations in the five fraction is, Residual fraction > organic matter – bound > .Fe- Mn oxide-bound > exchangeable fraction >carbonate – bound. The presence of high concentration of Ni in the study area may be as a result of the indiscriminate spilling of petroleum products (e.g. gasoline, diesel etc) and lubricating oil on bare ground by auto – mechanics in the area.

Cadmium: Cd has 58 % of its total concentration in the non-residual (bio – available) geochemical phases. The order of the concentrations in the five fractions is, Residual fraction >organic matter – bound fraction > Fe – Mn oxide – bound fraction > carbonate – bound fraction > exchangeable fraction. This order is slightly different from the order obtain by some other workers [41, 46, 47] in which they found the highest concentration of Cd in the Fe-Mn oxide bound fraction. The main difference is that the residual fraction has the highest concentration of cadmium. This is followed by the organic matter-bound (17.2 %) and Fe-Mn oxide – bound fraction (16.4 %). The difference between this two is very small. This means that there is adsorption of Cd to amorphous and crystalline Fe oxide but the process appears not to have been completed since much of Cd entering the soil in this area are of recent deposits, hence much of it is still in the organic matter – bound fraction.

Cd is a serious pollutant in this area because the concentration is high and a large proportion of its concentration is in bio-available (non-residual) geochemical phases. This portend great danger to human and animal health which are part of the food chain which have plants which takes in this metal at its base (or bottom). Cd competes with and displaces Zn in a number of Zn-metalloenzymes by irreversibly binding to the active sites, thereby destroying normal metabolism [4, 48]. A disease caused by Cd known as 'itai-itai' is rheumatic in nature and affect the bones adversely and conditions can become fatal.

This indicates the fairly high level of anthropogenic input of these metals into the environment of the study area. Cd, Pb and Ni are metals which can be derived from used lubricating oils and used batteries which form a high proportion of the discarded materials in the Auto-mechanic villages. Although the concentrations of the metals did not decrease outwardly from the mechanic village, it can be argued that the area which is in the mangrove/rain forest region and has experienced much amount of rain which will have pollutants in a particular area easily carried from one spot to another, distributed evenly within a radius around the place where pollution occurs by storm runoff water. The area can thus be said to be polluted with respect to cadmium as a result of the presence of the auto-mechanic village in the area.

The results of the calculation of mobility factor showed that the four trace metals have the following mobility factors:

Cu = 6.86 %, Pb = 13.9 %, Ni = 11.98 % and Cd = 21.17 %. The mobility factors of the metals are generally low with the exception of Cd with a mobility factor of 21.17 % which is moderately high.The relatively high concentrations of Cd in the study area coupled with this moderately high mobility factor puts Cd to be a serious pollutant in this area. This will make Cd ions more easily bio-available to plants which are at the bottom of the food chain which involve humans and higher animals. Human health may be at risk from Cd pollution in this area.

The results for pH and the four trace heavy metals determined in the present study were compared with results obtained for corresponding parameters in polluted sites elsewhere in similar studies. Some of the values obtained were comparable with those for these other sites while other values for the study area were either higher or lower than values obtained for these other sites. The average concentration of Cu in the study area, 102±18 $mgkg^{-1}$ (87.1 – 120 $mgkg^{-1}$) is comparable with result obtained for Baia Mare (femuziu site) in Romania (6.50 – 1730 $mgkg^{-1}$) [49] but is higher than results obtained for other sites, Metropolitan city of Lagos soil (0.10 – 2.90 $mgkg^{-1}$) [50], Niger Delta (28.3±32 $mgkg^{-1}$) [30], Udege tin/columbite mining are (0.34 $mgkg^{-1}$) [51], Karachi urban soil (33.3±12.8 $mgkg^{-1}$) [52] and Guadao oil-polluted region (18.4 $mgkg^{-1}$) [53].

The average concentration of Pb in present study area 68.5±9.9 $mgkg^{-1}$ (51.3 – 77.5 $mgkg^{-1}$) is comparable with results obtained for Karachi urban soil (42.1±55.8 $mgkg^{-1}$) [52] and Guadoa oil-polluted region in China (20.3 $mgkg^{-1}$) [53] but is much lower than results obtained for Niger Delta 9895±420 $mgkg^{-1}$) [30] and Baia mare area (Femeziu site) (115.0 – 19195 $mgkg^{-1}$) [49]. It is much higher than results obtained for metropolitan city of

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Lagos soil (0.02 – 0.23 $mgkg^{-1}$) [50] and Udege tin/columbite mining area (0.20 $mgkg^{-1}$) [51]. The average concencentration of Cd, 35±10 $mgkg^{-1}$ (20.1 – 42.7 $mgkg^{-1}$) is comparable with results obtained for Baia Mare area (Femeziu site) (0.15 – 113 $mgkg^{-1}$) [49]. It is much higher than results obtained for Niger Delta (1.3±1.0 $mgkg^{-1}$) [30], Obiobi/Obrikom oil spillage site (<0.20 $mgkg^{-1}$) [18], Udege tin/columbite mining area (ND) [51] and Gudao oil polluted region (0.19 $mgkg^{-1}$) [53]. It is lower than result obtained for Southwest China lead/zinc smelting area (75.4 $mgkg^{-1}$) [54]. The average concrntration of Ni, 121±51 $mgkg^{-1}$ (51.3 – 77,5 $mgkg^{-1}$) is much higher than results obtained for any of the areas listed in Table 11. The average pH of study area soil 6.40±0.58 (5.94 – 6.51) is comparable with result obtained for Baia Mare (Femeziu site) (5.7 – 7.5) [49 but lower than result obtained for Gudao oil-polluted region (7.3 – 8.05) [53]. The soil in the study area is slightly acidic.

Table 1: Average Concentration of Four Metals in soil and pH of soil in the study area, control area and the different Locations (sampling sites)

Parameters	Study Area average	Control Area Average	Study Area Sampling Stations				
			Site I	Site II	Site III	Site IV	Site V
Copper (mg/kg)	102 ± 18	13.8 ± 1.6	89 ± 12	109 ± 22	105 ± 17	104 ± 20	105 ± 14
Lead (mg/kg)	68.5 ± 9.9	8.9 ± 1.6	65.5 ± 8.3	70.1 ± 8.9	70.6 ± 12	75 ± 7.2	62 ± 10
Nickel (mg/kg)	121 ± 51	15.7 ± 3.0	154 ± 20	48.5 ± 4.3	158 ± 7.1	159 ± 7.5	80 ± 35
Cadmium (mg/kg)	35 ± 10	5.39 ± 1.31	35 ± 12	22.6 ± 5.9	31.6 ± 3.9	43.2 ± 7.6	41.1 ± 40
pH	6.40 ± 0.58	6.66 ± 0.63	6.61 ± 0.48	5.89 ± 0.41	6.86 ± 0.36	6.32 ± 0.54	6.22 ± 0.67

Table 2: Average concentration of four metals and pH in six seasons

Parameters	**First Dry Season**	**First Rainy Season**	**Second Dry Season**	**Second Rainy Season**	**Third Dry Season**	**Third Dry Season**
Copper (mg/kg)	**102 ± 16**	**102 ± 19**	**102 ± 20**	**103 ± 18**	**99±17**	**104±19**
Lead (mg/kg)	**69.7 ± 6.9**	**69 ± 11**	**71.8 ± 9.6**	**64 ± 11**	**66±10**	**66±13**
Nickel (mg/kg)	**20 ± 55**	**118 ± 53**	**119 ± 52**	**126 ± 56**	**116±52**	**126±49**
Cadmium (mg/kg)	**32 ± 11**	**35 ± 10**	**36 ± 12**	**33.5 ± 9.8**	**36±11**	**33.6±8.1**
pH	**6.50±0.57**	**6.35±0.56**	**6.35±0.63**	**6.3± 0.65**	**6.45±0.54**	**6.31±0.54**

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Table 3: Comparison of Average Concentration of Metals in Five Sampling Sites with Guideline Values for Land uses of the Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health (CCME, 1999)

Parameters	Land Use				Locations				
	Agricultu-ral	Residential/Pa-rkland	Comm-ercial	Indus-trial	Site I	Site II	Site III	Site IV	Site V
Copper (mg/kg)	63	63	91	91	89 ± 12	109 ± 22	105 ± 17	104 ± 20	105 ± 14
Lead (mg/kg)	70	140	260	600	65.5 ± 8.3	70.1 ± 8.9	70.6 ± 12	75 ± 7.2	62 ± 10
Nickel (mg/kg)	50	50	50	50	154 ± 20	48.5 ± 4.3	158 ± 7.1	159 ± 7.5	80 ± 35
Cadmium (mg/kg)	1.4	10	22	22	35 ± 12	22.6 ± 5.9	31.6 ± 3.9	43.2 ± 7.6	41.1 ± 40
pH	6 to 8	6 to 8	6 to 8	6 to 8	6.61 ± 0.48	5.89 ± 0.41	6.86 ± 0.36	6.32 ± 0.54	6.22 ± 0.67

Table 5: Comparison of Results with Four other Soil Quality Guidelines.

Guideline	Cu (mg/kg)	Pb (mg/kg)	Ni (mg/kg)	Cd (mg/kg)	References
Norway	100	50.0	30.0	1.00	Reinmann et al.[55]
Netherland (action level)	190	530	210	12.0	Reinmann et al. [55]
EGASPIN Target Values	36.0	85	35.0	0.80	[35]
EGASPIN Intervention values	190	530	210	12.0	[35]
Guidelines for SPDC EIA process (acceptable ranges)	5-50	5-50	5-50	0.7-3.0	[40]
Switzerland (guide value)	50	50	-	0.8	FOEFL [56]
Site I	89 ± 12	65.5 ± 8.3	154 ± 20	35 ± 12	Present study
Site II	109 ± 22	70.1 ± 8.9	48.5 ± 4.3	22.6 ± 5.9	Present study
Site III	105 ± 17	70.6 ± 12	158 ± 7.1	31.6 ± 3.9	Present study
Site IV	104 ± 20	73 ± 7.2	159 ± 7.5	43.2 ± 7.6	Present study
Site V	105 ± 14	62 ± 10	80 ± 35	41.1 ± 40	Present study

Table 6: Average % Concentration of metals in Geochemical Phases.

Geochemical Phases	Copper	Lead	Nickel	Cadmium
Exchangeable %	2.14 ± 0.94	10.8 ± 3.6	3.14 ± 0.76	11.6 ± 3.5
Carbonate – bound %	4.8 ± 2.8	3.1 ± 1.4	8.9 ± 5.7	12.5 ± 6.9
Fe – Mu Oxide bound %	7.4 ± 6.4	12.6 ± 5.6	10.5 ± 4.4	16.4 ± 7.9
Organic matter-bound %	20.3 ± 8.5	12.6 ± 6.0	19 ± 10	17.2 ± 4.3
Residual %	66.5 ± 7.7	61.1 ± 8.6	59 ± ± 20	42 ± 13

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Table 7: Contamination/Pollution (C/P) index of each metal in each of of the sampling stations using the average value of each metal for the four seasons for the sampling stations

Sampling Stations	Contamination/Pollution (C/P) Index			
	Cu	Pb	Ni	Cd
Site I	2.47	0.77	4.4	43.8
Site II	3.03	0.82	1.39	28.3
Site III	2.92	0.83	4.51	39.5
Site IV	2.89	0.88	4.54	54.0
Site V	2.92	0.73	2.29	51.4

Table 8: Significance of interval of contamination/pollution (C/P) Index (Lacatusu, 1998)

C/P Index	Significance	Symbol
<0.1	Very slightly polluted	v.s.l
0.10 – 0.25	Slightly contaminated	s.l
0.26 – 0.50	Moderate contamination	m.l
0.51 – 0.75	Severe contamination	St. l
0.76 – 1.00	Very severe contamination	v.st.l
1.1 – 2.0	Slight pollution	s.p.
2.1 – 4.0	Moderate pollution	m.p.
4.1 – 8.0	Severe pollution	st.p.
8.1 – 16.0	Very severe pollution	v.st.p.
➢ 16.0	Excessive pollution	e.p.

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www.jabe.in **Vol.2.Issue.1.2015, E-ISSN:2394-2606**

Table 11: Results from the study compared results from similar studies elsewhere

River/Land Area	country	pH	Cu (mg/kg)	Pb (mg/kg)	Ni (mg/kg)	Cd (mg/kg)	References
Metropolitan city of Lagos	Nigeria	-	0.10 – 2.90	0.02 – 0.23	-		[50]
Niger Delta	Nigeria	-	28.3±32	895±420	43±20	1.3±1.0	[30]
Baia Mare Area (Femeziu Site)	Romania	5.7 – 7.5	6.5 - 1730	115.0 - 19195	0.2 – 29.3	0.15 - 113	[49]
Obiobi/Obrikom oil spillage Site	Nigeria	-	-	0.32 – 0.80	0.53 – 18.0	< 0.20	[18]
Udege Tin/Columbite Mining Area	Nigeria	-	0.34	0.20	0.04	ND	[51]
Southwest China Lead/Zinc Smelting Area	China	-	-	2485	-	75.4	[54]
Gudao oil-polluted Region	China	7.3 – 8.05	18.4	20.8	26.3	0.19	[53]
Karachi Urban Soil	Pakistan	--	33.3±12.8	42.1±55.8	-	-	[52]
Effurun Mechanic village area	Nigeria	6.40±0.58 (5.94 – 6.51)	102±18 (87.1 – 120)	68.5±9.9 (51.3 – 77.5)	121±51 (71.3 – 133)	35±10 (20.1 – 42.7)	Present study

CONCLUSION

Analysis of four metals Cu, Pb, Ni and Cd and the comparison of results with soil quality guideline values has shown that soil in all the sites have average concentration of copper higher than guideline values for Agricultural and Residential/Parkland. All sites also have average values of Cadmium higher than the guideline values for all land uses (i.e. Agricultural, Residential/Parkland, Commercial and Industrial land uses). The soil of study area is thus polluted with respect to cadmium. The result of the sequential extraction experiment also confirms that the study area soil is polluted with cadmium since a higher proportion of its concentration is in the bio-available non-residual fractions. The results of sequential extraction experiment also showed that the proportion of the concentration of lead and nickel in the available non-residual fraction is on the increase. The mobility factor of Cd is also moderately high, This can result in faster uptake of Cd ions by plant roots in the

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Area. Environmental authorities should make sure that areas such as this (e.g. Mechanic villages) should be well monitored to ensure that those working in this area conform to environmentally friendly behaviours such as not indiscriminately spilling petroleum products or lubricating oil oils in their surroundings.

ACKNOWLEDGEMENT

The Warri Refining and Petrochemical Company Ekpan-Warri is here acknowledged for making its facilities and equipment available for parts of this study. The Department of Chemistry, Delta State University Abraka, Delta State Nigeria is also acknowledged for contributing to the success of this study in terms of making available its facilities and reagents to the study.

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