JASEM ISSN 1119-8362

Full-text Available Online at
www.ajol.info and
www.bioline.org.br/ja

J. Appl. Sci. Environ. Manage. *Sept 2013*
Vol. 17 (3) 425-430

Comparative study of Heavy Metals Distribution in a Mechanic Workshop and a Refuse Dumpsite in Oluku and Otofure Benin City, Edo State, Southwestern Nigeria.

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Key word: *Comparative, Heavy Metals, Mechanic, Workshop, Refuse, Dumpsite*

ABSTRACT A comparative study of heavy metals; Lead, Chromium, Arsenic, Nickel, Cadmium and Mercury distribution was carried out in Oluku and Otofure both in Metropolitan Benin City, Edo State Nigeria with the view to determine the level of concentration and contribution of each site investigated. Thirty eight (38) soil samples were collected from and around mechanic workshop in Oluku and refuse dumpsite in Otofure at depths of 0 - 0.15m to 0.15 - 0.30m. They were carefully labelled in polythene bags and then taken to the laboratory for digestion and analysis using Atomic Absorption spectrometer (AAS). The results obtained were subjected to statistical treatment at $P < 0.05$ at 95% confidence level; the ultimate results were presented in mean ± SD. A correlation coefficient range (r) of 0.63-0.94 at $P < 0.001$ two tailed was obtained suggesting a high relationship between the elements in the soil. By comparison, the results obtained show that mechanic workshop contributes more of the heavy metals assessed in the environment except for Cadmium whose concentration was found to be slightly higher in the refuse dumpsite.@JASEM

http://dx.doi.org/10.4314/jasem.v17i3.12

The study was conducted in two (2) locations; Oluku and Otofure both in Ovia North-East Local Government Area of Edo State, Nigeria. Oluku is a commercial/satellite town located on latitude 06^0 27' 4.8"N and longitude 005' 53.5"E which is experiencing the influx of migrants from and around Benin City, because of its strategic position with natural vegetation. Otofure on the other hand is about one kilometer away from Oluku and located on latitude 06^0 27' 44.6"N and longitude 005^0 36' 03.9"E.

Interest has most recently been stimulated in researches at evaluating the levels of heavy metals around refuse dumpsite due to the growing concerns expressed by the government, regulatory agencies and the pubic over the large acres of land covered by the dumpsites. Feign et al (1991), Tiller (1992). Heavy metal is often generally referred to as a silent killer and was defined by Harmsen (1977) as those having density greater than 5g cm^{-3}, but most often denote metals that are toxic such as Pb. As, Hg, Ni, Se, and Se. During the 1980s, the risks of young children suffering from neuropsychological effects because of excessive Lead (Pb) ingestion appeared to be more serious than had been previously recognized, Needlemann et al; (1990). Therefore, heavy metal analysis form an important component tool needed to regulate environmental impact assessment in towns and cities, Asuen et al; (2005). Numerous studies have been carried out on assessment of environmental pollution during the last two decades and the results reveal that mining, oil spillage, solid waste, household, industrial effluent, automobile exhaust, combustion of fossil fuels etc. which finally settle in the soil constitute the major sources of heavy metals in sediments and soil, Browning (1969), Ndiokwere (1984), Page and Gange (1979) and WHO (1972) . Soil is very important in ecosystem research as it is the place where many types of interactions take place between minerals, air, water and biota. In the recent, the soil system has been subjected to physical stress by input of foreign substances such as heavy metals (Ukpebor et al; (2003).

As a result of ineffective law enforcement agencies to enforce existing environmental laws coupled with lack of stringency even when attempts are made to enforce, Nigerian citizens and indeed residents of Oluku and environs in Edo State continue to dump refuse and litter the environment indiscriminately with such toxic substances as condemned engine oil, car batteries from mechanic workshop and solid waste even on the streets. These heavy metals can become a threat to vegetation and animals and ultimately affects the quality of human life, Harrison (1982). Several mechanic workshops (both large and small) as well as solid waste dumpsite exist in the area of study. The purpose of this research is to compare the level of heavy metals; lead, chromium, Arsenic, Nickel, Cadmium and Mercury from a gigantic heavy duty mechanic workshop and a huge open solid waste dumpsite so as to establish whether the land can still be used for industrial/commercial and agricultural activities if the land is eventually reclaimed.

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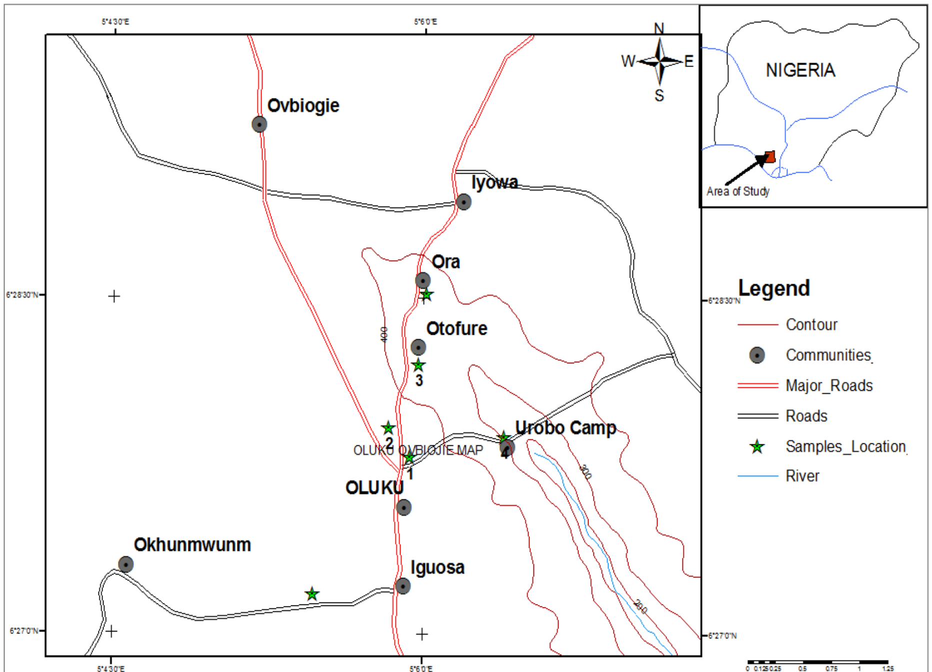

FIG. 1: MAP OF STUDY AREA SHOWING THE SAMPLED LOCATIONS

MATERIALS AND METHODOLOGY

Thirty eight (38) samples were collected from field, eighteen (18) were collected from and around mechanic workshop while the other eighteen (18) were collected in and around refuse dumpsite at depths of 0-0.15m-0.30m. Two (2) of the samples were collected at a distance of one (1) kilometer away as control point to show the degree of dispersion from the source. The samples were stored in polythene bags and taken to the laboratory to be air dried for three (3) days. They were then ground in an agate mortar and sieved through a 2mm nylon sieve. 0.5g of the processed sample was weighed in 250cm^{-3} hard glass (conical flask) digestion tube. About 10ml of concentrated Nitric acid ($HN0_3$) was added which produced effervescence. There after 5ml of perchloric acid ($HCLO_4$) was added and heated for about one (1) hour in an electric heater. The colour was observed to change to white and the content was allowed to cool for thirty (30) minutes. Subsequently 20 percent (%) diluted Hydrochloric acid (HCl) was added and filtered into 120ml container and diluted to volume with distilled water according to Allen et al., (1974). The concentrations of the heavy metals were determined using Atomic Absorption spectrometer (AAS) model solar 969 Unican series with Air Acetylene flame.

Data Analysis: The results are presented in mean ± SD (Standard deviation), analysis of variance (ANOVA) Peason's Correlation with Duncan multiple range at $P<0.05$ (95%) confidence level using SPSS.

RESULTS AND DISCUSSION

The statistical and analytical results of the parameters determine in this study are presented in Tables 1-5 with explanations.

Table 1: Effect of distance and depth of soil on the concentration of heavy metals in and around Heavy duty mechanic workshop

Element	Depth(m)	Distance (m) 0	1000	SEM
Cr (mg kg^{-1})	0 – 0.15	60.50 ± 0.01 $^{a}_{A}$	10.13 ± 0.06 $^{a}_{B}$	0.02
	0.15 – 0.3	56.20 ± 0.01 $^{b}_{A}$	9.92 ± 0.03 $^{b}_{B}$	0.01
	SEM	0.00	0.03	
Cd (mg kg^{-1})	0 – 0.15	37.40 ± 0.01 $^{a}_{A}$	12.17 ± 0.06 $^{a}_{B}$	0.02
	0.15 – 0.3	30.71 ± 0.01 $^{b}_{A}$	12.12 ± 0.03 $^{b}_{B}$	0.01
	SEM	0.00	0.03	
Ni (mg kg^{-1})	0 – 0.15	38.81 ± 0.01 $^{a}_{A}$	10.10 ± 0.00 $^{a}_{B}$	0.00
	0.15 – 0.3	25.30 ± 0.02 $^{b}_{A}$	10.03 ± 0.06 $^{a}_{B}$	0.02
	SEM	0.00	0.02	
Pb (mg kg^{-1})	0 – 0.15	82.58 ± 0.13 $^{a}_{A}$	11.62 ± 0.03 $^{a}_{B}$	0.05
	0.15 – 0.3	79.41 ± 0.01 $^{b}_{A}$	11.35 ± 0.21 $^{a}_{B}$	0.09
	SEM	0.05	0.09	
As (mg kg^{-1})	0 – 0.15	22.41 ± 0.01 $^{a}_{A}$	5.46 ± 0.11 $^{a}_{B}$	0.05
	0.15 – 0.3	18.59 ± 0.02 $^{b}_{A}$	5.35 ± 0.05 $^{a}_{B}$	0.00
	SEM	0.00	0.05	
Hg (µg kg^{-1})	0 – 0.15	7.50 ± 0.01 $^{a}_{A}$	0.30 ± 0.00 $^{a}_{B}$	0.07
	0.15 – 0.3	6.30 ± 0.01 $^{b}_{A}$	0.30 ± 0.00 $^{a}_{B}$	0.02
	SEM	0.00	0.05	

Means ± SD of the same column with similar superscript lowercase alphabet (aa or bb) are not significantly different while those with dissimilar superscript lowercase alphabet (ab or ba) are significantly different at P<0.05

Means ± SD of the same row with similar subscript uppercase alphabet (AA or BB) are not significantly different while those with dissimilar subscript uppercase alphabet (AB or BA) are significantly different at P<0.05

SEM: Standard minimum error to declare significance and it is calculated as √(EMS/nr) where EMS is the Error Mean Square and nr is the number of variables.

Table 2: Effect of distance and depth of soil on the concentration of heavy metals in and around Otofure Dumpsite

Element	Depth(m)	Distance (m) 0	1000	SEM
Cr (mg kg^{-1})	0 – 0.15	50.30 ± 1.00 $^{b}_{A}$	30.30 ± 0.01 $^{a}_{B}$	0.04
	0.15 – 0.3	37.71 ± 0.01 $^{a}_{A}$	21.00 ± 0.01 $^{b}_{B}$	0.01
	SEM	0.40	0.02	
Cd (mg kg^{-1})	0 – 0.15	38.91 ± 0.01 $^{b}_{A}$	22.60 ± 0.00 $^{a}_{B}$	0.02
	0.15 – 0.3	26.61 ± 0.01 $^{a}_{B}$	15.50 ± 0.82 $^{b}_{A}$	0.00
	SEM	0.00	0.04	
Ni (mg kg^{-1})	0 – 0.15	27.31 ± 0.01 $^{b}_{A}$	14.70 ± 0.02 $^{a}_{B}$	0.01
	0.15 – 0.3	17.90 ± 0.01 $^{a}_{B}$	12.20 ± 0.03 $^{b}_{A}$	0.03
	SEM	0.00	0.00	
Pb (mg kg^{-1})	0 – 0.15	49.41 ± 0.01 $^{a}_{A}$	20.40 ± 0.01 $^{a}_{B}$	0.01
	0.15 – 0.3	32.71 ± 0.01 $^{b}_{B}$	18.30 ± 0.00 $^{b}_{A}$	0.00
	SEM	0.00	0.01	
As (mg kg^{-1})	0 – 0.15	13.92 ± 0.02 $^{a}_{A}$	13.50 ± 0.02 $^{a}_{B}$	0.0
	0.15 – 0.3	10.40 ± 0.03 $^{b}_{A}$	10.20 ± 0.01 $^{b}_{B}$	0.01
	SEM	0.00	0.03	
Hg (µg kg^{-1})	0 – 0.15	2.02 ± 0.03 $^{a}_{A}$	1.50 ± 0.01 $^{a}_{B}$	0.01
	0.15 – 0.3	1.19 ± 0.02 $^{b}_{A}$	1.20 ± 0.00 $^{b}_{A}$	0.02
	SEM	0.00	0.01	

Means ± SD of the same column with similar superscript lowercase alphabet (aa or bb) are not significantly different while those with dissimilar superscript lowercase alphabet (ab or ba) are significantly different at P<0.05

Means ± SD of the same row with similar subscript uppercase alphabet (AA or BB) are not significantly different while those with dissimilar subscript uppercase alphabet (AB or BA) are significantly different at P<0.05

SEM: Standard minimum error to declare significance and it is calculated as √(EMS/nr) where EMS is the Error Mean Square and nr is the number of variables

Table 3: Summary of the differences and % differences of heavy metals concentration in topsoil and subsoil in and around mechanic workshop and refuse dumpsite in the area of study.

Element	Depth (m)	Mechanic Workshop Distance (m) 0	Refuse Dumpsite Distance (m) 0	Differences in conc.	% Difference in conc.
Cr (mg kg^{-1})	0-0.15	60.50 ± 0.01	50.30 ± 1.00	10.0	9.2
	0.15-0.30	56.20 ± 0.01	37.71 ± 0.01	18.49	19.69
Cd (mg kg^{-1})	0-0.15	37.40 ± 0.01	38.91 ± 0.01	1.51	1.98
	0.15-0.30	30.71 ± 0.01	26.61 ± 0.01	4.10	7.15
Ni (mg kg^{-1})	0-0.15	38.81± 0.01	27.31 ± 0.01	11.50	17.40
	0.15-0.30	25.30 ± 0.02	17.90 ± 0.01	7.40	17.13
Pb (mg kg^{-1})	0-0.15	82.58 ± 0.13	49.41 ± 0.01	33.17	25.13
	0.15-0.30	79.41 ±0.01	32.71 ± 0.01	46.7	41.65
As (mg kg^{-1})	0-0.15	22.41 ± 0.01	18.92 ± 0.01	8.49	23.37
	0.15-0.30	18.59 ± 0.02	10.40 ± 0.01	8.19	28.25
Hg (mg kg^{-1})	0-0.15	7.50 ± 0.01	2.20 ± 0.01	5.48	57.56
	0.15-0.30	6.30 ± 0.01	1.19 ± 0.02	5.11	68.22

Table 4: Permissible limit of heavy metals in Agricultural, Residential and Commercial/ Industrial soils as adopted by three countries

Country	As (mg/kg)	Cd (mg/kg)	Cr (mg/kg)	Pb (mg/kg)	Ni (mg/kg)	Hg (µg/kg)
Germany	50	5	500	1000	200	20000
*Canada	30	3	750	200	150	800
Taiwan	60	5	250	500	200	2000

* Limit used for this work

Culled from Regulatory standard of heavy metal pollutants in soil and ground water in Taiwan by Lee and Lee, (2011)

Table 5: Correlation between elements in soils at both locations

	Cr	Cd	Ni	Pb	As	Hg
Cr	1.00	0.93 ***	0.92***	0.88***	0.75***	0.67***
Cd		1.00	0.85***	0.72***	0.73***	0.63***
Ni			1.00	0.88***	0.66***	0.64***
Pb				1.00	0.69***	0.68***
As					1.00	0.94***
Hg						1.00

P<0.05=* is poorly significant
P<0.01=** is significant
P<0.001=*** is highly significant
P>0.05=NS Not Significant

***Discussion*: Chromium:** the highest level of chromium was obtained in and around the heavy duty mechanic workshop with a concentration value of 60.50 ± 0.01mg kg $^{-1}$ kg in the top soil at depth 0-0.15m and 56.20 ± 0.01mg kg $^{-1}$ was recorded for subsoil of depth 0.15m-0.30m. There was a significant decrease from top soil to subsoil in and around the mechanic workshop and at a distance of one kilometer away. At the refuse dumpsite, 50.30 ± 1.00 mg kg^{-1} was recorded in the topsoil while 37.71 ± 0.01mgkg $^{-1}$ was recorded in the subsoil. When the value obtained was compared to Canadian, German and Taiwan permissible limit, it was noted that the soil can still be used for both industrial/commercial purpose as well as agricultural usage. The correlation coefficient between chromium and other elements/metals shows a positive correlation range r=0.67-0.93 at P < 0.001 two (2) tailed. (Table 5).

Cadmium: Cadmium has a value of 38.91 ± 0.01 mg kg^{-1} at the refuse dumpsite for topsoil and 26.61 ± 0.01mg kg $^{-1}$ for subsoil and at the mechanic workshop, the values of 37.40 ± 0.01mg kg^{-1} and 30.71 ± 0.01mg kg^{-1} for top and subsoil respectively. It is important to state here that the value obtained from both sites and at a distance away from the sites were far above the permissible limit of 3mg kg^{-1} for agricultural use, thereby rendering the land/soil useless for agricultural purpose unless a serious remediation is done before usage. However, the land/soil can be used effectively for industrial/commercial purposes since the level recorded were far below the permissible limit (table 4). Correlation of Cadmium with other elements in the soils shows a positive correlation range (r) 0.63-0.85 at P < 0.001 (99%) two tailed suggesting a similar origin.

Nickel: With reference to tables 1 and 2, Nickel was found to be higher (table 1) in mechanic worship with a concentration of 38.81 ± 0.01mg kg^{-1} at depths of 0.15m and 25.30±0.02mg kg-1 at depths of 0-0.15, 0.30m which is higher than the one obtained from the refuse dumpsite 27.31 ± 0.01mg kg^{-1} and 17.90 ± 0.01mg kg^{-1} respectively. It should be noted that both soils can still be used for industrial/commercial as well as for agricultural purposes. The correlation coefficient between Ni and other elements range between 0.64-0.88 at $P < 0.001$ 2 tailed or 99 percent significance.

Lead: The highest level of lead was found to be 82.58 ± 0.13 mg kg^{-1} on the topsoil in and around mechanic workshop. The level of concentration decreased with depth and distance. The contribution of the refuse dumpsite was far below that of the mechanic workshop by 25.13% (table 3). This higher percentage difference could be due to the fact that lead is a component of petrol additives and its increase is inferred as the possible causes of lead in the soil, Asuen et al., (2005). Other factors could be traced to condemned car batteries deposited, panel beating as well as welding and fabrication activities on the site. Lead was strongly correlated at $P < 0.001$ two (2) tailed. Despite the difference between the highest value obtained from the mechanic workshop 82.58 ± 0.13 mg kg^{-1} and that obtained from the refuse dumpsite 49.41 ± 0.01 mg kg^{-1} (table 3), they were found to be below recommended permissible limit for industrial/commercial purposes as well as that of soil in agricultural practice (table 5).

Arsenic: Arsenic with the chemical formula (As) was also found to be more concentrated in and around mechanic workshop with a concentration of 22.41 ± 0.01 mg kg^{-1} at the topsoil while that of the refuse dumpsite was found to be 13.92 ± 0.02 mg kg^{-1}. Generally, the distribution pattern seems to be the same for all heavy metals assessed. For industrial, commercial and agricultural uses, arsenic was found to be below the permissible limit compared to the standard used in this work (table 5)

Mercury: The percentage difference obtained between mechanic workshop and refuse dumpsite was found to be 68.22 (table 5) this result clearly shows that one of the major sources of anthropogenic mercury in the environment is from the activities of mechanic workshop owners. The implication of this could be attributed to the Nigerian Crude oil which has a high concentration of Iron, Copper, Zinc, Pb and Hg, Osibanjo and Kakulu (1983). From the foregoing, the activities of mechanic workshop owners need to be properly monitored, otherwise, some day there will be disease epidemics and serious environmental threat.

Summary: The ultimate results obtained from the study area revealed that the concentration of the heavy metals assessed decreased from top to subsoil in and around and at a distance away from the sample location (Table 1&2). The results also show that the sources of the heavy metals were anthropogenic; this was further buttressed by the strong positive correlation between the soils. Tables 1, 2 & 3 show that the highest concentrations of all the metals under investigation were from the mechanic workshop except for cadmium with a slight increase of about 1 percent from the refuse dumpsite. The study also shows that the Mechanic workshop is one of the major sources of anthropogenic heavy metals concentration in the environment and its contribution far exceeds that from other sources, Njoku and Ngene (2012) supports this. The result obtained from this work was found to be higher than Ukpebor et al; 2003 while Ukpebor et al; 2003 was found to be higher than Ihenyen (1998b). This suggests that human population which has been increasing is a fundamental factor that enhances heavy metal contribution to the environment.

If the trend of human population increase continues without proper check by way of legislature and enforcement, there may soon be an epidemic of disease and a serious environmental degradation in the area and indeed in other areas where related practices are being carried out in Nigeria. Cadmium in the soil was found to be higher than 3mg kg^{-1} permissible limits (Table 5) for agriculture. However, the soils are still usable for domestic, commercial/industrial purposes.

By and large, mechanic workshop owners and dumpsite managers should be given stringent rules to operate with full compliance in order to minimize the level of heavy metals introduced to the environment. Further studies on speciation and concentration are encouraged by researchers in this area of investigation.

Acknowledgement: The authors will like to acknowledge Prof. M.A Bamikole of the Animal Science Department, Faculty of Agriculture, University of Benin, Benin City, for the statistical work and Martlet Environmental Research laboratory Limited for the AAS analysis.

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