Assessment of Some Heavy Metals as Contaminants in Petroleum Contaminated Soils of Eleme, Port Harcourt Nigeria

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Abstract— *Samples from petroleum contaminated soil of Eleme, Port Harcourt and from non petroleum contaminated soil, Awka, Nigeria serving as control were analyzed for heavy metals. The results of the analysis showed that the metals concentrations in mg/kg were Ni <0.05- 2.05, Cr 0.005- 0.37, Cd <0.005- 0.008, Zn 0.14 – 2.87 Pb <0.02- 0.19 Fe 12.32-29.11, Mn < 0.008- 0.036, Se <0.001, as <0.001, and V <0.001. Majority of the metal concentrations were above those of the control. Though the values obtained did not exceed soil quality standards stipulated in the Environmental Management Regulations, 2007, the toxic metals could accumulate to a threatening level over a period of time. Food poisoning, occupational hazards and various disorders emanate from heavy load of toxic metals in our environment.*

Keywords— *Heavy Metals as Contaminants, Petroleum Contaminated Soils, Port Harcourt, soil quality, toxic metals.*

I.   INTRODUCTION

Environmental pollution may result from industrial and commercial activities when substances resulting from these activities enter the environment and attain levels which may cause discomfort and / or harm to man and his environment (Udosen *et al*, 1990). From the point of view of environmental pollution, metals may be broadly classified into three categories namely, non-toxic but accessible, toxic but non-accessible and toxic and accessible .It is the third category that has attracted more attention from the point of view of environmental pollution and public health (Dara, 2008).

The toxic metals occur in very small quantities in the earth's crust (less than 1000ppm) and hence are called "trace metals". These are further arbitrarily subdivided on the basis of their densities. Those having densities below $5g/cm^3$ are called light metals and those with densities above $5g/cm^3$ are designated as heavy metals (Dara, 2008; Santra, 2005). The main threats to human health from heavy metal (HM) are associated with exposure to cadmium, lead, mercury and arsenic but additionally, there are other 19 elements known as heavy metals: antimony, bismuth, cerium, chromium, cobalt, copper, gallium, gold, iron, manganese, nickel, platinum, silver, tellurium, thalium, tin, uranium, vanadium and zinc (Fernandez-lugueno *et al*.,2013). Some heavy metals are essential for living organisms but high concentrations or accumulation in a physiological system is detrimental or injurious to health especially where such metals are found above maximum allowable levels (Hough et al., 1982; Nigerian Industrial Standard (NIS), 1983). Large amounts of any of them may cause acute or chronic toxicity referred to as poisoning (Kabata-Pendras and Mucherjee, 2007).Heavy metals accumulate in topsoil and at larger concentrations can poison important soil microbial groups, crops and food (Chaudri, 2001). In areas with high concentrations, metallic contamination of food and water probably led to the poisonings (Gilman et al., 1975). A disaster resulting from heavy metal contamination was the minamata disease in Japan caused by methyl mercury poisoning (Christian *et al*, 1974). The mercury poison was through food chain build-up which occurred in Japan's minamata bay which received industrial waste containing mercury compounds.

Moriber (1974) reported that the consumption of waste water from a mine which produced cadmium, zinc and lead resulted in rickets-like disease called itai-itia.

Heavy metal toxicity can result in brain damage or the reduction of mental processes (Gaza *et al*.,2005) and central nervous function (Bouchard *et al*.,2011), lower energy levels (Holmstrup et al.,2011), damage to DNA (Jomova *et al*., 2011), alterations on the gene expression (Salgado-Bustamante *et al*., 2010) , Skin (Burger et al., 2007), muscle (Visnjic-jeftic *et al*.,

2010), liver (Burger et al.,2007), heart (Otles and Cagindi,2010) and other vital organs for humans and other living organisms.

Long term exposure to heavy metals may result in slowly progressing physical muscular and neurological degenerative processes that mimc Aizheimer's disease, Parkinson's disease, muscular dystrophy, multiple sclerosis (Jones and Miller, 2008), gangrene, diabetes mellitus, hypertension and ischemic heart disease (Otles and Cagindi, 2010). Other consequences are allergies and cancer (Dietert and Piepenbrink, 2006).

The emergence of the industrial age and large scale mining brought occupational diseases caused by various toxic metals. Metallic constituents of pesticides and therapeutic agents (e.g antimicrobials) were additional sources of hazardous exposure. The burning of fossil fuels containing heavy metals and the addition of tetra ethyl lead to gasoline has now made environmental pollution the major source of heavy metal poisoning (Gilman *et al.*, 1975). Petroleum substances are contaminants that most frequently occur in the water-soil environment and can pollute environment through leaking pipelines, oil spill storage facilities, (Okop and Ekpo, 2012). Metals leached from eating utensils and cookware also increase the risk of heavy contamination (Gilman et al., 1975). Heavy metal contamination of urban top soil has been of great concern as regards to their harmfulness, persistence and non- degradability in the environment (Al-Chalabi and Hawker, 2000, Onianwa, 2001; Ameh, 2014). Unfavourable effects of high concentrations of heavy metals to soil functions, soil microbial community composition and microbial growth have long been distinguished under both field and laboratory conditions (Dara, 2018; Chaudri, 2001).

Nature and Distribution levels of Toxic Metals in wastewater from some small scale business in Ibadan Metropolis has been conducted (Adejumobi, 2005). Crude oil contamination of soil occurs frequently in various ways and in certain areas. It will be of great value if the levels of toxic metals in the petroleum contaminated soils are established as these would serve as guide to control of this pollution and hence metal poisoning.

II.   MATERIALS AND METHODS

2.1   Study Area

Eleme coordinates are 4.7994^{o}N, 7.1198^o E. It is located at east of Port Harcourt and covers an area of 138km^2. At 2006 census, it had a population of 190,884. Precipitation in Port Harcourt averages 2708mm and the average annual temperature is 26.4^{o}C. The average annual relative humidity is 71.0% (https//weather and climate.com). Awka is found in the south eastern part of Nigeria. It is the capital of Anambra State and is located on Latitude 6°09′N and Longitude 7°12′E. The climate is tropical with an annual rainfall of about 11,450mm, average temperature of 28°C and relative humidity of 91% at dawn (Nwangwu, 2015).

2.2   Soil Sampling

Composite samples of top soil more than 1kg were collected from six locations at o-12cm with the aid of a hand auger and measuring tape (Voutsa, 1996; Nwankwoala and Ememu, 2018). Five out of the six samples were petroleum contaminated soils from Eleme Port Harcourt Nigeria and one was non- petroleum contaminated soil from Awka Nigeria. The non-petroleum contaminated soil was serving as control. Care was taken to wash and clean the auger before sampling each location in order not to contaminate the samples. The samples were transferred into pre-labeled polythene bags after which they were transported to the laboratory for preservation, digestion and analysis.

2.3   Sample Preservation

Samples were stored in the laboratory fridge at 4°C prior to digestion and analysis.

2.4   Sample Digestion

Conventional aqua regia digestion was performed in 250ml glass beakers covered with watch glasses. A well mixed sample of 0.5000g was digested in 12ml of aqua regia (3:1 mixture of HCl and HNO$_3$ on a hot plate for 3hrs at 110°C. After evaporation to near dryness, the sample was diluted with 20ml of 2%(v/v) dilute nitric acid and transferred into a 100ml volumetric flask after filtering through Whatman No 42 paper and diluted to 100ml with DDW (Chen and Ma, 2001).

2.5   Sample Analysis

Heavy metal contents of each digest were determined using an Atomic Absorption Spectrophotometer (Schimadzu AA 670) as described in APHA (2000). Soil sample was aspirated into an air/acetylene or nitrous oxide/acetylene flame generated by a

hollow cathode lamp at a specific wavelength peculiar only to the metal programmed for analysis. For each metal analyzed, standards and blanks were prepared and used for calibration before samples were aspirated. Concentration and specific absorbance appeared for each metal in each sample. The concentrations were recorded and printed out for all the samples. Limit of detection was set at <0.001mg/L. Metals determined from the soil samples were reported in mg/kg.

III.   RESULTS AND DISCUSSION

Table 1 shows levels (mg/kg) of heavy metals in the various samples analyzed.

TABLE 1
METAL CONTENT OF SOIL SAMPLES IN MG/KG

	V	Ni	Cr	Cd	Zn	Pb	Fe	Se	Mg	Ca	Mn	As
Sample A	<0.001	<0.05	0.009	<0.005	2.70	<0.02	22.87	<0.001	0.86	0.18	0.008	<0.001
Sample B	<0.001	2.05	<0.05	<0.005	0.47	0.14	12.32	<0.001	0.31	0.14	0.011	<0.001
Sample C	<0.001	<0.05	0.010	<0.005	2.87	0.16	20.67	<0.001	0.11	0.11	0.036	<0.001
Sample D	<0.001	0.15	0.37	0.008	1.24	0.15	29.11	<0.001	0.09	0.04	0.008	<0.001
Sample E	<0.001	0.15	0.009	0.008	0.36	0.19	27.46	<0.001	0.25	0.17	0.009	<0.001
Sample F	<0.001	0.33	0.008	<0.005	0.29	0.14	21.64	<0.001	0.41	0.14	0.015	<0.001
Sample G	<0.001	0.57	0.008	<0.005	0.14	<0.02	15.61	<0.001	0.52	0.13	0.013	<0.001
Soil Quality Standard (2007)	-	100	100	1	150	200	-	20	-	-	1800	1
NESREA Draft Effluent Standard for Petroleum Based & Allied Chemical Industries (2007)	-	0.5	0.1	0.5	2	0.5						

IV.   CONCLUSION

In order of decreasing magnitude, the average heavy metal content in the top soil samples are as follows: Fe (12.32-29.11)> Zn (0.14-2.87)>Ni (<0.05- 2.05)> Cr (<0.005-0.37)>Pb (<0.02-0.19)>Mn(<0.008-0.036)>Cd(<0.005-0.008)>V(<0.001), As(<0.001) and Se(<0.001). Majority of the metal concentrations were higher than control except Ni in samples A, C, D, E, F, Cr in sample B, Pb in sample A, Fe in sample B, Mn in samples A, D and E. All vanadium and arsenic concentrations fell below or equal to the detection limit. The average concentration of all the metals were compared with soil quality standards stipulated in the Environmental Management Regulations, 2007 and the results show that they were all within the standards. However, they could accumulate to a threatening level over a period of time (Gilman, 1975; Adejumobi, 2005).

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