British Journal of Environmental Sciences
Vol.4, No.3, pp.39-48, August 2016
Published by European Centre for Research Training and Development UK (www.eajournals.org)

ANALYSIS OF HEAVY METAL CONTAMINATION BY ARTISANAL REFINING PLANTS IN THE NIGER DELTA REGION, SOUTHERN NIGERIA

John D. Njoku[1], Toochukwu E.Ebe[2] and Akachukwu O. Enem[2]

[1]Dept. of Urban and Regional Planning, Federal University of Technology, Owerri, Nigeria
[2]Dept. of Environmental Technology, Federal University of Technology, Owerri, Nigeria

ABSTRACT: *Artisanal refining Plants are common features of the Niger Delta Region of Nigeria. The effects of heavy metal contamination on soil by non-conventional refining plants were investigated and analyzed using standard methods. Two soil samples were collected at 18 m intervals between Plants A and B and at 24 m intervals between Plant B and C. Then control sample was collected 2 km away from unimpacted soil. The result of the analysis showed that polynuclear aromatic hydrocarbon (PAH) recorded maximum concentration of 6899.4942 ppm at station C at the depth of 0-15 cm. Furthermore, the concentration of heavy metals investigated are below critical levels as proposed by FEPA (1991) and NCC(1991).*

KEYWORDS: Artisanal Plants, Niger Delta, Nigeria, Hydrocarbon Contaminated, Heavy Metal

INTRODUCTION

The soil an ecosystem of its own is directly affected with the discharge of wastewater containing hydrocarbons, residual crude oil spillages from the source of the crude and resultant spilling of both crude oil and refined products during production and transportation. This causes various effects on both plants and microorganisms that are dependent on the nutrients inherent in the soil for survival, it retards plants growth (Anoliefo et al,1994; Atuanya1987) reduces aeration by blocking pores between soil particles hence create conditions of anaerobiosis (Rossel and Tarradellas,1991).

Crude oil once refined yields three basic grouping of products which are produced when it is broken down into fractions; gas and gasoline, middle distillates, and fuel oil and residue cuts (World Refining, 2010).

The term non conventional refining plant in the context and scope of this study will be referred to as a setup which involves the use of drums and pipes fitted together and mounted on a heat source so as to heat or distill the crude inside the drum to a certain temperature in order to produce some petroleum products. Amangbara and Njoku (2012) described it as an artisanal refining and "*Kpo Fire*" by the locals, is a local way of distilling crude oil to get diesel as refined product. It typically involves primitive illegal means in which crude oil is boiled and the resultant fumes are collected, cooled and condensed in tanks to be used locally for lighting, energy or transport (UNEP, 2011).

A non conventional refining plant is not concerned with the chemical changes in crude oil rather it involves the physical changes found in simple distillation. It has been reported that petroleum refining contributes to solid, liquid and gaseous wastes in the environment (Nwankwo et al,1998).

The ability of soil to perform any of the identified functions depends on it physical, biological and chemical attributes while the realization of the performance is conditioned by natural and anthropogenic factors. All these functions are time dependent. Humans, amongst the most influential players, indirectly alter the performance characteristics of soil, thus limit or enhance its capacity to function (Carter, 2002).

MATERIALS AND METHODS

Delimitations and description of study area Bodo community lies on the coastal low land of the Niger Delta, and in the Southern part of Gokana Local Government Area of Rivers State. The community is about 56 kilometers by road from Port Harcourt, the capital of Rivers State. It is located between latitude $4^{0}36^{1}$N and longitude $7^{0}21^{1}$E of the equator (Taneen, 2005). The major occupations of the people are fishing and farming.

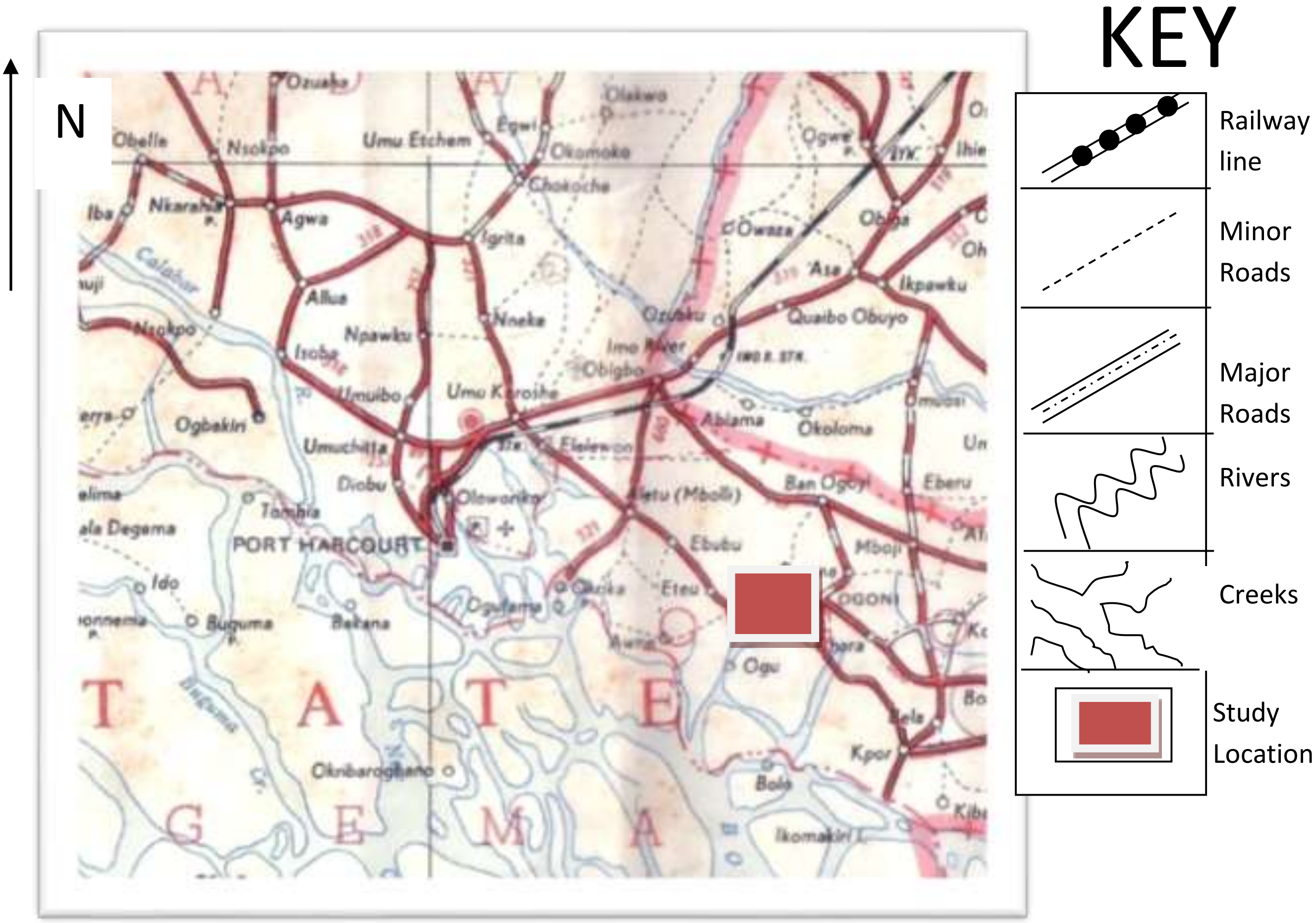

Figure 2.1 Schematic drawing of parts of Rivers State showing the study site, BodoIn Gokana Local Government Area Rivers state.

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DETERMINATION OF TOTAL PETROLEUM HYDROCARBON AND POLYAROMATIC HYDROCARBON

Soil sample of 5g was weighed into the brown extraction container and conc. sodium sulphate (Na_2SO_4) was added to remove its water molecule. Then conc. Di-chloromethane (DCM) was added to extract the hydrocarbon content that was in the soil sample. Also, the solution was filtered through the funnel that was packed with cotton woo, Na_2SO_4 and Silica gel. Then the filtrate was passed through the silica column and collected in the beaker and then blown down the Nitrogen gas until it is finally evaporated. Before the extracted sample was ran in the Gas chromatography, the content in the evaporated beaker was mixed with 1ml of DCM before 1 micro liter (0.001 ml) was injected into the GC system with a syringe.

Furthermore, the heavy metals were determined using atomic adsorption spectrophotometer.

RESULTS AND DISCUSSION

Variations in PAH and TPH

Polyaromatic hydrocarbon (PAH) and Total Petroleum Hydrocarbon (TPH) varied from 37.6942 to 6899.4287 and 83.1469 to 21872.1149 respectively. These two parameters are hydrocarbons, and they have the highest range of 6861.7345 and 21788.9680 as shown in Table 3.1

Variations in Sand, Silt, Clay and pH

Mean and standard error values for sand, silt and clay are 68.2857 $\pm$ 2.21491, 10.7143 $\pm$ 1.01866 and 20.7143 $\pm$ 1.64560 respectively.

pH has a minimum and maximum values of 4.12 and 5.99 respectively.

Variations in Heavy Metals

Zinc, Copper, Nickel and Chromium varies from 3.692 to 34.691, 0.729 to 14.491, 2.691 to 11.421 and 1.896 to 7.147 respectively. However, Zinc has the highest range amongst all the heavy metals with 30.999 followed by Copper with 13.762, Nickel 8.730 and Chromium 5.251.

Arsenic has a minimum and maximum of 0.0010 to 0.0430 with a range of 0.0420 while Cadmium has a minimum and maximum variation of 0.0010 to 0.0441 and a range of 0.0431.

Mercury, Barium, Cobalt and Vanadium has a minimum and maximum variations of 0.0010 to 0.0037, 0.0010 to 0.0694, 0.0027 to 0.3370 and 0.0010 to 0.0213 respectively and their ranges are as follows 0.0027 for Mercury, 0.0684 for Barium, 0.3343 and 0.0203 for Cobalt and Vanadium respectively as would be seen in table 3.1.

Interactions of Heavy Metals with Hydrocarbons

Some of the heavy metals measured have significant interactions with hydrocarbons at $p<0.01$. PAH correlated positively with Lead ($r=0.886$), Copper ($r=0.846$), Arsenic ($r=0.860$), Zinc ($r=0.892$), Nickel ($r=0.754$) Chromium ($r=0.663$) and Mercury ($r=0.907$). TPH correlated positively with Lead ($r=0.921$), Copper ($r=0.885$), Arsenic ($r=0.859$), Zinc ($r=0.933$), Nickel ($r=0.769$), Chromium ($r=0.6770$) and Mercury ($r=0.879$) Table 3.2

Spatial Variations in Heavy Metals

Lead recorded maximum concentration of 4.329(mg/kg) in station II at the depth of 0-15cm and recorded minimum concentration of 0.0012(mg/kg) in the control station at the depth of 15-30cm. Copper recorded maximum concentration of 14.491(mg/kg) in station III at the depth of 0-15cm and a minimum concentration of 0.729(mg/kg) in control station at the depth of 15-30cm. Chromium recorded maximum concentration of 7.147(mg/kg) in station IV at the depth of 0-15cm and minimum concentration of 1.896(mg/kg) in the control station at the depth of 15-30cm. (Figure 3.1)

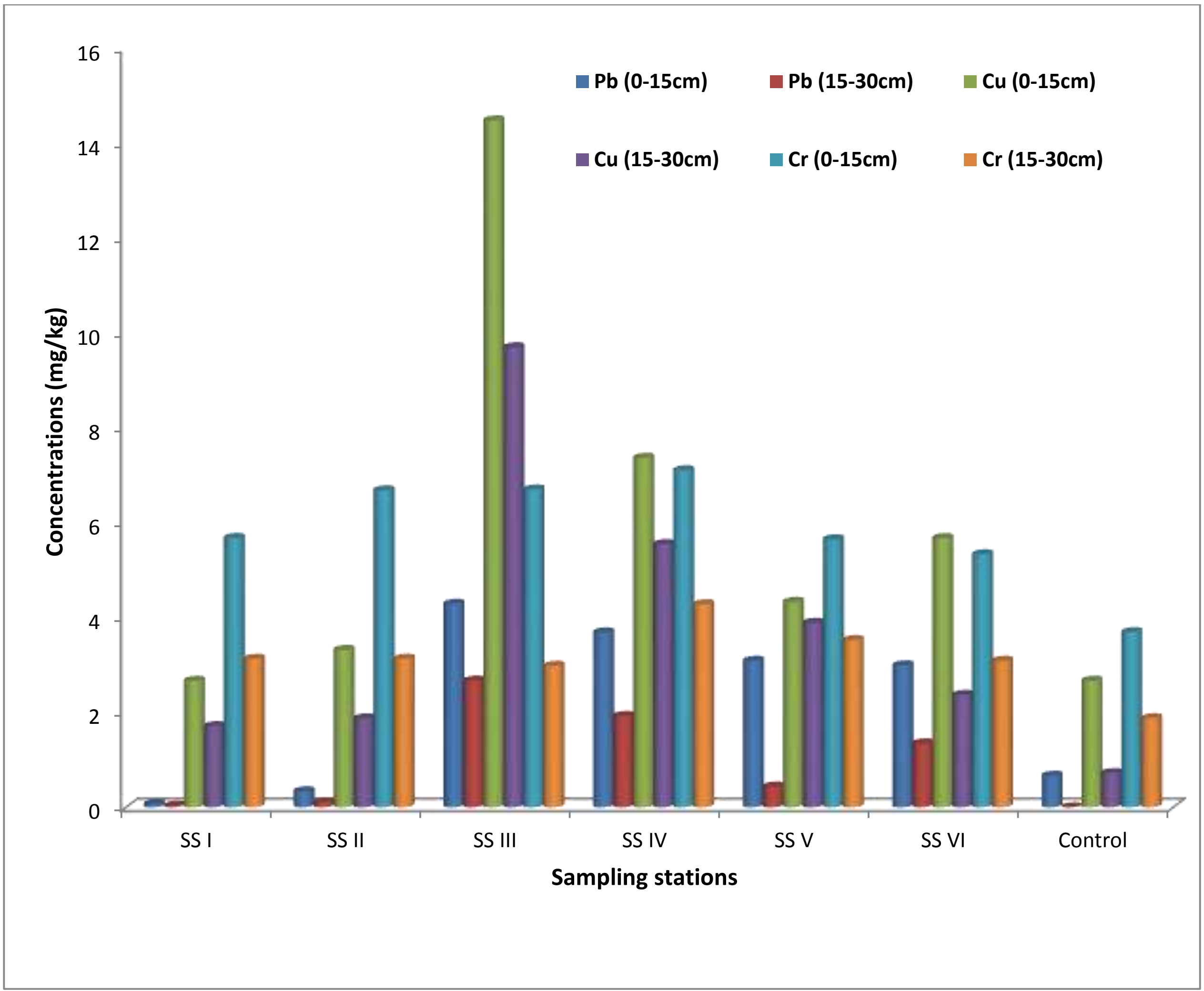

Figure 3.1 Spatial variations in levels of lead, copper and chromium contents of impacted soils of Bodo Community

Arsenic recorded maximum concentration of 0.043(mg/kg) in station III at the depth of 0-15cm and minimum concentration of 0.001(mg/kg) in station I and control station at the same depth of 15-30cm respectively (Figure 3.2). Maximum cadmium concentration of 0.0441(mg/kg) was recorded in station V at the depth of 0-15cm and minimum concentration of 0.001(mg/kg) in station VI and control stations respectively at the same depth of 15-30cm. Mercury recorded maximum concentration of 0.0037(mg/kg) in station V at the depth of 0-15 and minimum concentration I at the depth of 0-15 and 15-30cm, station II 0-15 and 15-30cm, station V 15-30cm and control station 0-15 and 15-30cm respectively (figure 3.2)

Zinc and Nickel maximum concentration was recorded in station III and IV 34.691(mg/kg) and 11.421(mg/kg) at the same depth of 0-15cm and minimum concentrations of 3.692(mg/kg) and 2.691(mg/kg) in the control station and at the same depth of 15-30cm respectively (Figure 3.3)

Maximum concentration of 0.0694 of barium was recorded in station V at the depth of 0-15 and the minimum of 0.001(mg/kg) was recorded at the control station at the depth of 15-30cm as shown in Figure 3.4

Spatial Variations In particle Size Composition

In the particle size composition, sand recorded maximum composition of 81% in sampling station VI at the depth of 0-15cm and a minimum composition of 48% in sampling station III at the depth of 0-15cm.

Silt recorded maximum composition of 19% in sampling station III at the depth of 0-15cm and a minimum composition of 5% in sampling station I at the depth of 15-30cm.

Clay recorded maximum composition of 33% in sampling station III at the depth of 0-15cm and minimum composition in sampling station VI at the depth of 0-15cm Figure 3.5

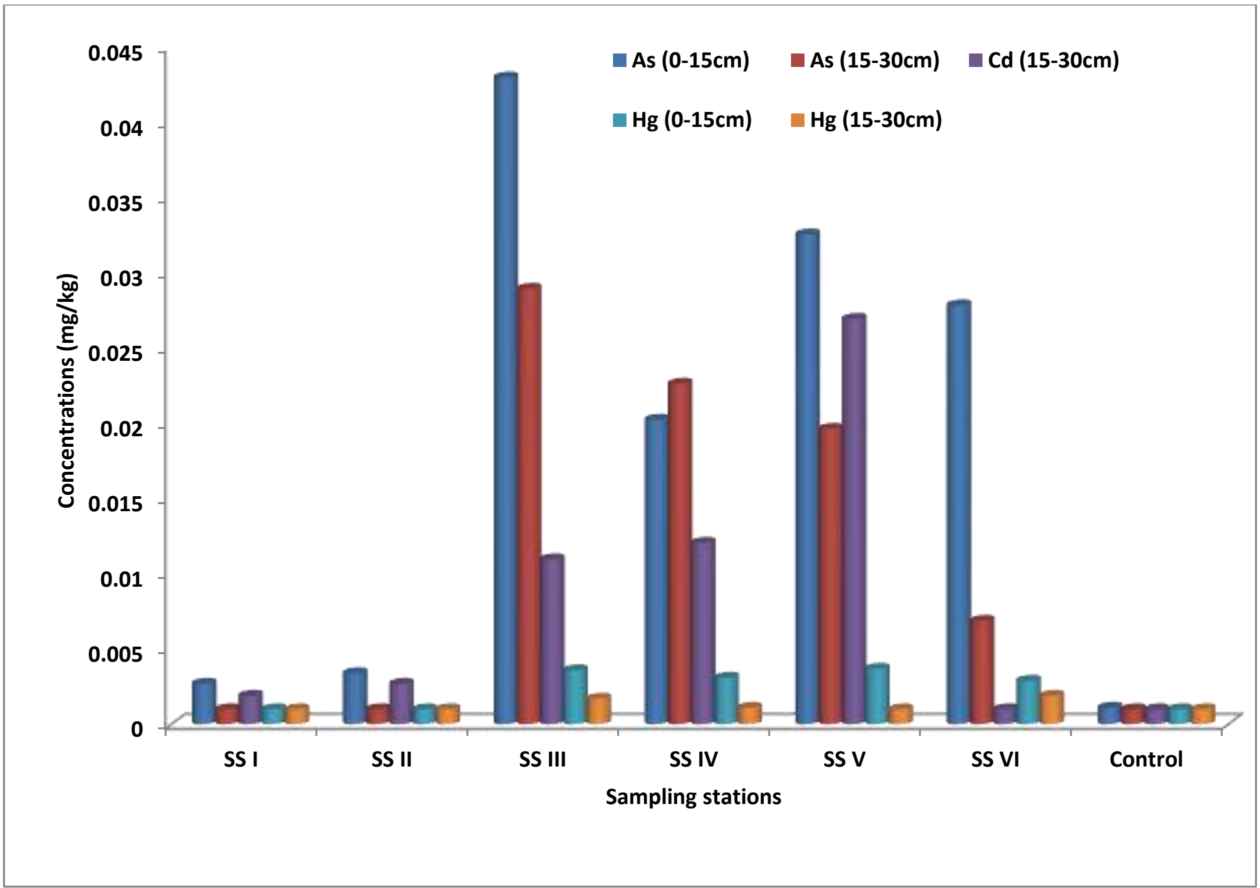

Figure 3.2 Spatial variations in levels of arsenic, cadmium and mercury contents of impacted soils of Bodo Community

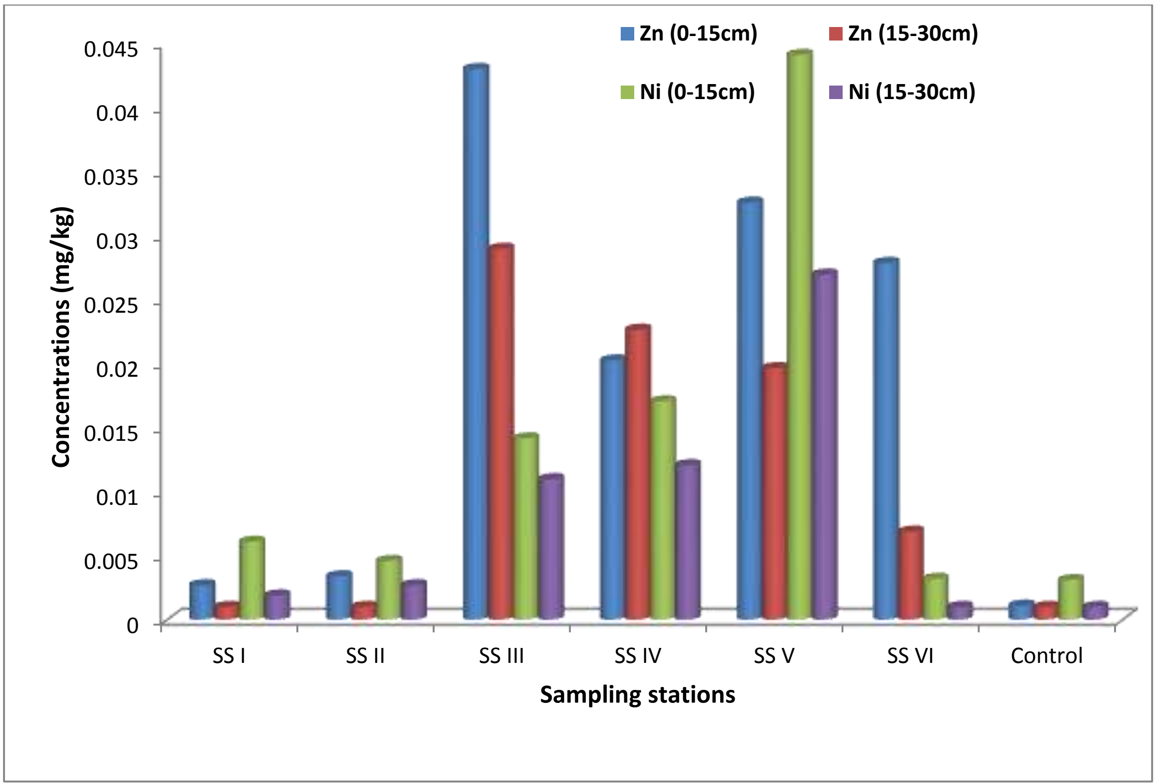

Figure 3.3 Spatial variation in levels of zinc and nickel contents of impacted soils of Bodo Community

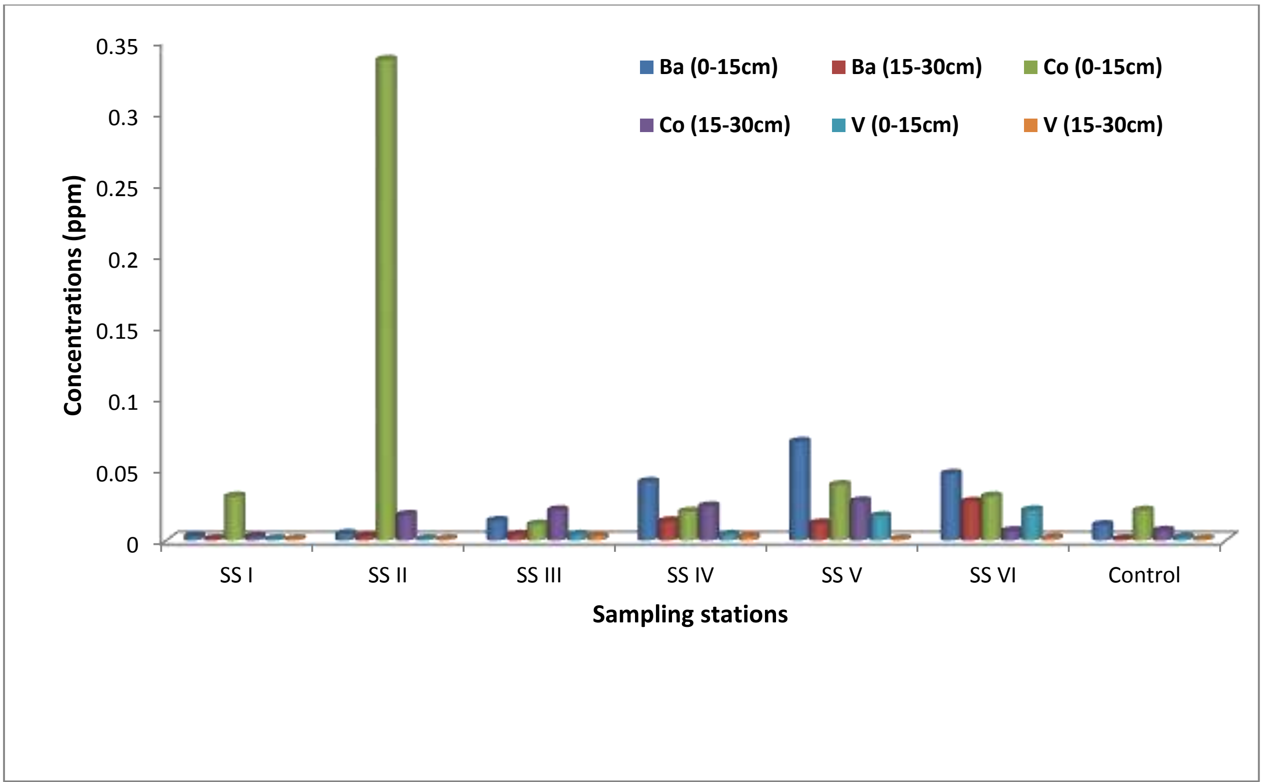

Figure 3.4 Spatial variations in levels of barium, cobalt and vanadium contents of impacted soils of Bodo Community

Table 3.1 Descriptive Statistics of the heavy metal Parameters of Impacted Soils in Bodo Community

Parameters	Minimum	Maximum	Range	Mean	SE
PAH	37.6942	6899.4287	6861.7345	1844.8400	534.9329
TPH	83.1469	21872.1149	21788.9680	5913.381529	1.71662003
pH	4.12	5.99	1.87	5.1179	0.13987
Sand	48.00	81.00	33.00	68.2857	2.21491
Silt	5.00	19.00	14.00	10.7143	1.01866
Clay	12.00	33.00	21.00	20.7143	1.64560
Lead	0.001	4.329	4.328	1.56110	0.412634
Copper	0.729	14.491	13.762	4.76550	0.990754
Arsenic	0.0010	0.0430	0.0420	0.015164	0.0038502
Zinc	3.692	34.691	30.999	12.355714	2.240971
Cadmium	0.0010	0.0441	0.0431	0.010650	0.0032636
Nickel	2.691	11.421	8.730	6.82493	0.633911
Chromium	1.896	7.147	5.251	4.52621	0.449024
Mercury	0.0010	0.0037	0.0027	0.001786	0.0002846
Barium	0.0010	0.0694	0.0684	0.018007	0.005558
cobalt	0.0027	0.3370	0.3343	0.042707	0.0228088
Vanadium	0.0010	0.0213	0.0203	0.004421	0.0017134

Table 3.2 Correlation (r) matrix between the heavy metals and Hydrocarbons

Parameters	PAH	TPH
pH	-0.654*	-0.614
Sand	-0.427	0.425
Silt	0.525	0.465
Clay	0.286	0.323
Lead	0.886**	0.921**
Copper	0.846**	0.885**
Arsenic	0.860**	0.859**
Zinc	0.892**	0.933**
Cadmium	0.513	0.404
Nickel	0.754**	0.769**
Chromium	0.663**	0.677**
Mercury	0.907**	0.879**
Barium	0.531	0.492
Cobalt	0.026	-0.080
Vanadium	0.473	0.445

*=significance at p<0.05, **=significance at p<0.01, EC= Electrical conductivity
TOC=Total organic carbon, TOM=Total organic matter, EX. Al=Exchangeable Aluminum

Ex=Exchangeable

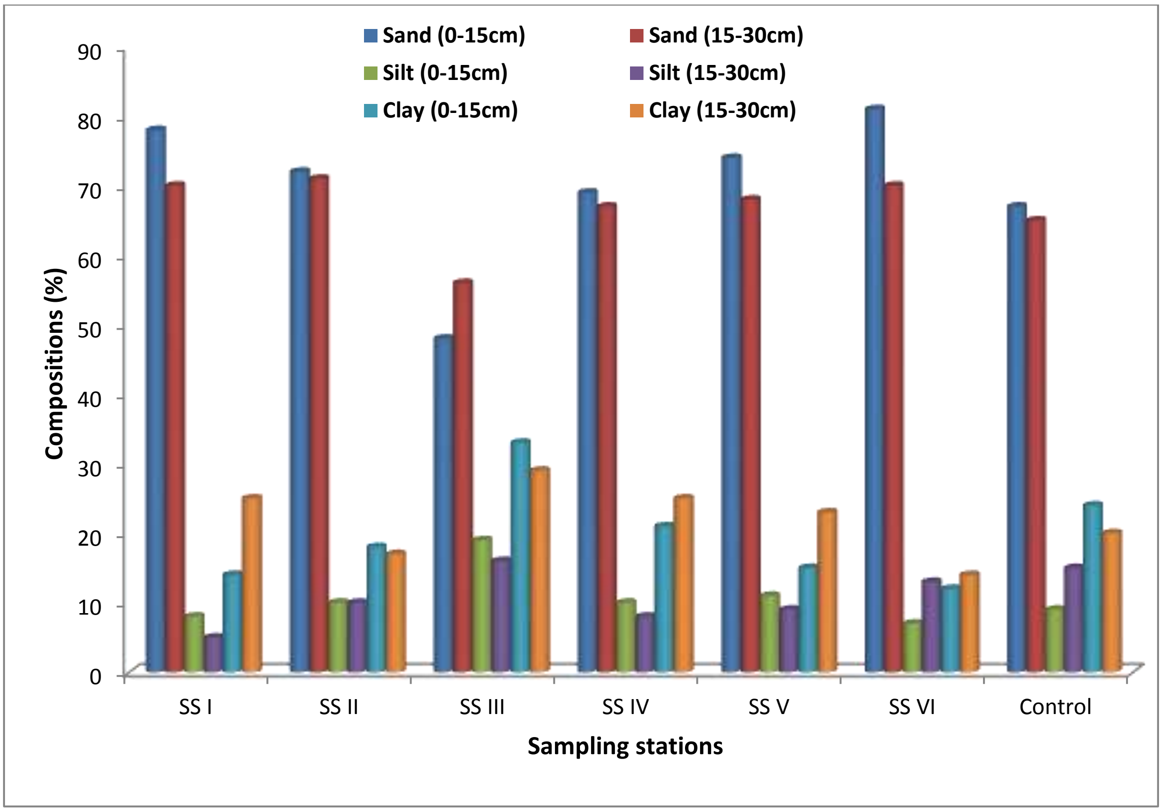

Figure 3.5 Spatial variations in levels of sand, silt and clay compositions of impacted and control soils of Bodo community.

Plate1 Non Conventional Refining Plant II at Bodo Community in Gokana Local Government Area

DISCUSSION

Maximum concentrations of cobalt and vanadium recorded 0.337(mg/kg) and 0.0213(mg/kg) in sampling stations II and VI respectively at the same depth of 0-15cm and minimum concentration of 0.01(mg/kg) in station I at the depth of 0-15 and 15-30cm, station II and V at the depth of 15-30cm.

The results from this study has revealed that there were different concentration of hydrocarbons and heavy metals within the impacted and control stations at different depths (0-15 and 15-30cm). The concentration of polynuclear aromatic hydrocarbon (PAH) and total petroleum hydrocarbons (TPH) showed that PAH recorded maximum concentration of 6899.4287ppm at station III at the depth of 0-15cm and minimum concentration of 37.6942ppm at control station at the depth of 15-30cm. TPH recorded maximum concentration of 21873.1149ppm in station III at the depth of 0-15cm and a minimum concentration of 83.1469ppm at the control station at the depth of 15-30cm. These figures represent high concentration of hydrocarbons when compared with the control station.

A review of the existing data on Niger Delta Environmental Survey NDES (1999), Osuji,(2001), Osuji et al (2004) and UNEP (2011) affirms that with such high concentration of hydrocarbons shows severe hydrocarbon contamination. BTEX were below detectable limit and it might be as a result of high volatility. It is suspected BTEX compounds might have volatilized during the destruction of the refining plants.

The results also showed that the whole area under investigation recorded highest pH value of 5.99 in control station at the depth of 0-15cm while minimum value of 4.12 was recorded at the depth of 0-15cm in sampling station III. This revealed that the soil of the study area were slightly acidic.

Particle size composition showed that the soil composition of the soil is mainly sandy. Sand ranges from 48% to 81% and a range of 33%. Clay ranges from 12% to 33% with range of 21% while silt ranges from 5% to 19%. The sandy nature of the soil of the study area aids infiltration of contaminants and increases the pollution pathway for contaminants. The texture also allows for free drainage and ease of mobility of ions within the soil.

Concentration of all the heavy metals is below critical levels proposed by FEPA (1991) and NCC (1991) to constitute hazard. Though Zn recorded the highest concentration at station III with the value of 34.691 at 0-15cm and minimum value of 3.692 at control station at the depth of 15-30cm

REFERENCES

Anoliefo, G.O and Nwiko, O.F (1994).Effects of Spent Lubricating Oil on the Growth of *Capsicum annum.L.*and*Lycopersiconesculatummiller*.Environmental Pollution in Delta State,Vol. 88 p361-374

Atuanya, E.I (1987). Effects of Waste Oil pollution on Physical and Chemical properties of the Soil. A Case Study of Waste oil Contaminated Delta Soil in Bendel..

Carla, W.M (2002) Environmental Geology Updated Edition McGraw-Hill Companies NY. New York.

FEPA (1991) Federal Environmental Protection Agency, (1995). Corporate Profile Garki, FCT, Abuja Nigeria

NDES (Niger Delta Environmental Survey) (1999). Phase I Report Vol.1 1-4. NDES Lagos, Nigeria.

Nwankwo, J.N and Irrechukwu, D.O (1998). Problems of Environmental Pollution and Control in the Petroleum Industry: The Nigerian Experience

Osuji,L.C;Inimfon,A.U; Ogali, R.E (2006). Attenuation of Petroleum Hydrocarbons by Weathering.A Case Study. Chem. Biodiv.3; 422-431

Rossel, D and Tarradellas, J. (1991).*Dehydrogenase* activity of Soil Microflora. Significance in Ecotoxicological Test. Environ. Toxicol. Soil Quality 6.17-21

United Nations Environmental programme (UNEP) (2011). UNEP Report on Ogoni Land. Nairobi, Kenya.

World Petroleum Refining (2009). MIT Massachusetts Institute of Technology Publications . Massachusetts USA