

*Full Length Research Paper*

# The effects of petroleum exploration and production operations on the heavy metals contents of soil and groundwater in the Niger Delta

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**Soil and water samples obtained from four sampling points; around an oil well head, flare site, waste pit and effluent discharge point in an exploration area in the Niger Delta were analysed for their heavy metals contents. The results showed that the amount of lead present in the soil ranges from 3.40 – 99.40 mg/kg, copper values were in the range of 5.10 – 49.30 mg/kg, Nickel concentration vary from 1.60 – 13.80 mg/kg, values for cadmium, iron, zinc, and chromium were 0.04 – 0.95 mg/kg, 536.00 – 12,872.00 mg/kg, 11.1 – 274.00 mg/kg and 1.30 – 165.00 mg/kg respectively. Apart from zinc and nickel, all other heavy metals were higher than the toxicity limits for heavy metals in natural soil; this implies pollution of the soil by heavy metals. Also the waters were found to be polluted by lead, the pH of the water samples was found to deviate significantly from DPR limits and W.H.O. standard for potable water. This also implies pollution.**

**Remediation measures were suggested so as to render the soil and ground water fit for use.**

**Key words:** Soil, water, heavy metals, pollution, exploration area, Niger Delta.

## INTRODUCTION

The petroleum industry is organized into four broad sectors: exploration and production of crude oil and natural gas; transport; refining; as well as marketing and distribution. This study addresses only exploration and production operations. The negative effects of the exploration and production operations in oil producing areas can be enormous. The impacts resulting from oil spills, drilling mud and fluid, formation waters and effluent discharge are of great concern because of their deleterious effects. Among the activities of geophysical exploration, the most significant negative effect on the physical and chemical condition of soil and groundwater is the sinking of drill holes and detonation of explosives within the hole. The explosion will disturb natural disposition of aquifer bodies and natural groundwater chemistry will be affected

as well.

Petroleum exploration and production companies use wide range of chemicals in their operations especially for well protection and in separation of water from oil. These chemicals can pollute the soil and groundwater system in the areas where such operations are being carried out if they are not properly controlled according to guidelines and standards set by regulating agencies like the Department of Petroleum Resources (DPR) and Federal Environmental Protection Agency (FEPA) now Federal Ministry of Environment.

Formation waters and effluents discharges are high essentially in total dissolved solids and some of the effluent discharges contain oil sheen and some chemicals injected into the wells to inhibit corrosion of equipment or enhance the separation of oil from water. Such water could have detrimental effects on plants and animals (Amatya et al., 2002). The side effect of petroleum activities can be severe. The problems range from soil degra-

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dition to pollution of surface water and groundwater. These problems often lead to lower land values and loss of certain land use capacities.

This work is aimed at assessing and establishing the contaminant status of the soil and groundwater in an exploration area in the Niger delta and possibly suggests ways of remediating such soil or water so that it can be useful to the inhabitants of that area.

## MATERIALS AND METHODS

### Tectonic evolution and framework

The Niger delta basin is an integral part of the sedimentary basins of southern Nigeria. It lays within longitude 4° and 9° East and latitude 4° and 6° North. It covers an area of about 75,000 sq km. It is bounded to the northwest by fault flexures which coincide with the up dip limit of Delta tectonics and to the east by the Cameroun volcanics. Tectonic elements such as the Anambra basin and the Abakaliki uplift bounds it to the north. The basin is open to the south (Stoneley, 1956). The axis of the basin is parallel to the continental-oceanic crust boundary.

### Study area

The study area is the X-field, which lies within a densely forested area with slot systems connected to Mayuku creek, which links up with Benin and Uton River.

The area is put into an industrial use (Petroleum producing firms abound in the area) farming and rural habitation. Land use classification was accomplished through field study, and the land use categories identified in the area of study are gullied sites, industrial sites, barren area and housing.

### Soil studies

Soil samples were taken at four point of interest. Thus;

- (a) Around oil well heads (SS<sub>1</sub>)
- (b) Flare sites (SS<sub>2</sub>)
- (c) Waste pit (SS<sub>3</sub>)
- (d) Effluent discharge point (SS<sub>4</sub>)

SS<sub>1</sub>, SS<sub>2</sub>, SS<sub>3</sub>, and SS<sub>4</sub> mean Soil Sample 1, 2, 3 and 4. respectively

The soils were taken at 0 – 15 cm for top soil, 15 – 30 cm for middle soil and 30 – 60 cm for bottom soil for heavy metals analysis.

## METHODS

### Heavy metals in soil

Soil samples were air dried and sieved through a 2 mm sieve. The fine earth was then used for the analysis. Particles larger than 2 mm mesh size were discarded. The heavy metal contents of soil were determined using the atomic absorption spectrophotometric method as described in Standard Methods (APHA, 1995; Ademoroti, 1996b). The heavy metal contents of soil were determined after dry ashing the soils and extracting with dilute nitric acids. An aliquot of the filtrate of the samples was taken (about 3-5 ml). Appropriate hollow cathode lamps were obtained and the AAS set to the appropriate wavelength as shown in the Table 1.

Iron, zinc, copper, chromium, cadmium, nickel and lead were

**Table1.** Wavelength of absorption for some heavy metals in atomic absorption spectrophotometer.

Metals	$\lambda$ (nm)
Iron	248.3
Copper	324.7
Cadmium	228.8
Chromium	357.9
Lead	283.4
Zinc	213.8
Nickel	232

determined by atomic absorption spectrophotometer (AAS) using air acetylene flame.

### Hydrogeological studies

The area of study is undulating lowland with a galloping terrain composed of alternating gullies. The hydrology consists of an intricate system of waterways; the study area is well drained by Mayuku creek, which bound the area in the northwest. The water table is high.

### Heavy metals in water

The heavy metal contents of water were determined using the atomic absorption spectrophotometric method as described in Standard Methods (APHA, 1995; Ademoroti, 1996b). The concentrations of the metals of interest were determined by direct reading from the spectrophotometer.

## RESULTS

The results are presented in Tables 1 - 4

## DISCUSSION

The results of heavy metal contents in soil are shown in Table 2. The results showed that heavy metals were present in considerable amount in the soil. This is so because of the wide use of chemicals containing heavy metals being discharged into the environment as a result of petroleum exploration and production activities. The amount of lead in soil of the sampled areas varies from 3.40 to 99.40 mg/kg. These values are higher than toxicity characteristic leachate limits (TCL) of 5.00 mg/kg for lead (Bowen, 1979). Lead is toxic to many plants species, although a few are relatively tolerant. When ingested, lead can cause a disease called plumbism; lead also is known to damage the brain, the central nervous system, kidney, liver and the reproductive system (Ademoroti, 1996a). Waste products from the use of chemicals like pipe lax, lube 106 and other lubricants like diesel oil which are used in the production of petroleum result in pollution of soils by lead. Natural occurring concentration by lead in soil ranges from 2 to 20.00 mg/kg

**Table 2.** Results of heavy metals content of soil in four sampling points viz; around oil well heads (SS<sub>1</sub>), Flare sites (SS<sub>2</sub>), Waste pit (SS<sub>3</sub>), and Effluent discharge point (SS<sub>4</sub>).

Sampling points	Dept (h) (cm)	Pb (mg/kg)	Cu (mg/kg)	Ni (mg/kg)	Cd (mg/kg)	Fe (mg/kg)	Zn (mg/kg)	Cr (mg/kg)
around oil well heads (SS <sub>1</sub> )	0 – 15	24.00	49.80	4.80	0.95	536.00	11.10	8.5
	15– 30	22.00	5.10	2.90	<0.05	1847.00	264.00	14.8
	30– 60	30.00	5.30	1.60	0.13	905.00	16.20	25.50
Flare sites (SS <sub>2</sub> )	0 – 15	99.40	16.70	6.70	<0.05	2995.00	66.70	159.00
	15– 30	3.40	11.20	3.50	0.23	1642.00	21.20	1.30
	30– 60	3.40	14.30	3.50	0.23	1642.00	21.20	1.30
Waste pit (SS <sub>3</sub> )	0 – 15	12.40	33.60	3.50	<0.05	1560.00	71.80	2.50
	15– 30	27.80	31.70	5.40	0.43	3610.00	153.00	2.90
	30– 60	7.50	30.60	4.10	0.33	1437.00	18.00	2.50
Effluent discharge point (SS <sub>4</sub> )	0 – 15	52.90	32.10	7.40	0.33	4183.00	97.10	157.00
	15– 30	61.90	12.50	0.64	0.82	12,872.0	163.00	165.00
	30– 60	38.30	36.70	13.80	0.74	10741.0	163.00	77.80

All values are mean values of triplicate determinations

**Table 3.** Results of heavy metals content of water in four sampling points viz; around oil well heads (SS<sub>1</sub>), flare sites (SS<sub>2</sub>), waste pit (SS<sub>3</sub>), and effluent discharge point (SS<sub>4</sub>).

Bore hole No.	Lead Pb <sup>2+</sup> (mg/l)	Copper Cu <sup>2+</sup> (mg/l)	Nickel Ni <sup>2+</sup> (mg/l)	Cadmium Cd <sup>2+</sup> (mg/l)	Total Iron Fe <sup>2+</sup> , Fe <sup>3+</sup> (mg/l)	Zinc Zn <sup>2+</sup> (mg/l)	Chromium Cr <sup>6+</sup> (mg/l)	pH
BH <sub>1</sub>	0.44	<0.005	<0.05	<0.005	<0.01	<0.01	<0.005	3.80
BH <sub>2</sub>	0.31	<0.005	<0.05	<0.005	<0.01	<0.01	<0.005	4.50
BH <sub>3</sub>	0.35	<0.005	<0.05	<0.005	0.01	0.01	<0.005	3.30
BH <sub>4</sub>	<0.05	<0.005	<0.05	<0.005	0.017	<0.01	<0.005	5.00

All values are mean values of triplicate determinations. BH<sub>1</sub>, BH<sub>2</sub>, BH<sub>3</sub>, and BH<sub>4</sub> means bore-holes 1, 2, 3 and 4 respectively.

**Table 4.** DPR (1991), WHO (1971) and FEPA (1991) limits/standard for potable and Domestic water for some parameters.

Parameters	DPR limits	WHO Standard	FEPA limits
Lead (Pb <sup>2+</sup> )	0.05mg/l	0.01- 0.05mg/l	0.05mg/l
Copper (Cu <sup>2+</sup> )	1.00mg/l	1.00 – 1.5mg/l	1.00mg/l
Nickel (Ni <sup>2+</sup> )	-	-	0.01mg/l
Cadmium (Cd <sup>2+</sup> )	-	0.01mg/l	0.01mg/l
Total Iron (Fe <sup>2+</sup> and Fe <sup>3+</sup> )	1.00mg/l	0.3mg/l	0.3mg/l
Zinc (Zn <sup>2+</sup> )	1.50mg/l	5.0 - 15mg/l	5.0mg/l
Chromium (Cr <sup>6+</sup> )	0.03mg/l	0.05mg/l	0.05mg/l

(Bowen, 1979). The concentration level of copper ranges from 5.10 to 49.80 mg/kg, these values are relatively higher compared to the normal range of 5.00–20.00 mg/kg required by plants in natural soil concentration (Bowen, 1979). Copper is generally higher in soil derived from igneous rocks and tends to be lower in extreme acid

and alkaline soil. Copper in excess amount can be harmful and pollution occurs in areas where copper are found and worked, e.g about 3.9 million tones of copper (IV) oxide are released into the atmosphere in United States of America due to smelting of copper ores (Giddings, 1973). Nickel concentration level vary from 1.60 to 13.80

mg/kg, it falls within the normal range of 2.00 to 750.00 mg/kg in natural soil concentration (Bowen, 1979).

The concentration of cadmium in soils of the study area ranges from 0.04 to 0.95 mg/kg. Naturally occurring cadmium concentration ranges from 0.03 to 0.30 mg/kg. Therefore cadmium concentration in the soil analysed is far above the naturally occurring range, this is pollution especially when cadmium is known to be one of the most harmful pollutant. Cadmium is known to cause itai-itai disease; (Jun, 1969; Jun 1974; Gustav, 1974; Ademoroti, 1988)

The results of soil samples analysis for iron calls for concern because of the relatively high values, it ranges from 536.00 to 12,872.00 mg/kg. Iron toxicity rarely creates problems in the field. Although groundwater table in the area is shallow and the iron could find its way to the groundwater thereby polluting it. Iron was found to have infiltrated greatly up to 60 cm depth in the soil horizons. The high iron concentration could be as result of;

The natural occurrence in the soil,

- (ii) Iron from chemicals waste such as D 76 (weighting agent) which is one of the chemicals used for drilling operation and
- (iii) Iron contained in the laterite soil used in sand filling the waste pits after completion of the drilling operation.

The amount of zinc in the sampled soil vary from 11.1 to 264.00 mg/kg, these levels are within the natural range of 1.00 to 900 mg/kg in soil (Bowen, 1979). Zinc is an essential element in our diet. Too little zinc can cause problems, but too much zinc is also harmful. Harmful effects generally begin at levels 10 - 15 times higher than the amount needed for good health. Large doses taken by mouth even for a short time can cause stomach cramps, nausea, and vomiting. Taken longer, it can cause anemia and decrease the levels of your good cholesterol. It is not known if high levels of zinc affect reproduction in humans but rat that were fed large amounts of zinc became infertile (U.S. DPHHS, 2005). Inhaling large amounts of zinc (as dusts or fumes) can cause a specific short-term disease called metal fume fever.

Zinc can be a pollutant, especially in areas close to industrial plants engaged in processing of petroleum, because zinc is directly added to the drilling fluids as zinc carbonate and act as corrosion inhibitor for mud formations and part of the zinc can be trapped by the soil layer (Katherine, 1985)

The chromium values range from 1.30 to 165.00 mg/kg in excess of the toxicity characteristics leachate procedure limits of 5.00 mg/kg. Chromium (VI) is toxic. Acute toxic effects occur when breathing very high levels of chromium (VI) in air, which can damage and irritate your nose, lungs, stomach, and intestines. People who are allergic to chromium may also have asthma attacks after

breathing high levels of either chromium (VI) or (III). Long term exposures to high or moderate levels of chromium (VI) cause damage to the nose (thereby resulting in bleeding, itching, and sores) and lungs. Ingesting very large amounts of chromium can cause stomach upsets and ulcers, convulsions, kidney and liver damage, and even death. It is not known if chromium harms humans but mice that ingested large amounts of chromium had reproductive problems and offspring with birth defects.

Results in Table 3 show that the pH of the water samples from the four boreholes sampled (BH<sub>1</sub>, BH<sub>2</sub>, BH<sub>3</sub> and BH<sub>4</sub>) were 3.80, 4.50, 3.30 and 5.00, respectively. These values are highly acidic and below the standard of 6.5 – 8.5 recommended by World Health Organisation and Department of Petroleum Resources for potable water (WHO, 1971; DPR, 1991). Table 3 also shows the level of heavy metals present in the ground water in the exploration site. From the result, it is observed that only lead was found to be above W.H.O and DPR standards. This could be dangerous for the users of such waters as lead is known to cause plumbism, and damages to the brain, the central nervous system, kidney, liver and the reproductive system (Ademoroti, 1996a).

### Significance of results

The results obtained in this study indicate that some heavy metals occurred above the natural occurring values, their occurrence at such levels indicates pollution of the sampling points in the studied area.

The surface soil samples of the following sampling points, flare site area, wells D and E, waste pit, around well head G suggest pollution by heavy metals lead, copper, chromium, iron, nickel, and zinc. Although some metals are considered to be of essential importance for plant growth, they can cause harmful effect when in excess (for example) zinc levels in the soil studied are higher compared to the limits, crops grown on such soil may suffer from leaves and retarded growth and translocation of iron in the plant.

Copper occurs in levels above normal range of 5.00 to 20.00 mg/kg (Bowen, 1979) required for plant growth, high levels of copper caused grey node symptoms on plant grown on agricultural soils with excess amount of copper.

The heavy metals contained in these soils could have emanated from drilling fluids components of mud, diesel, bit lube, caustic lignosulphonate, a water-based drilling mud thinner which contains chrome, ferrochrome and spilled hydrocarbon from drilling operations.

The ground water samples show evidence of heavy metals contamination, the heavy metals occurring in most of the samples was lead and iron for BH<sub>1</sub>, which is in the vicinity of the flow station and flare site. The lead contamination of virtually all the boreholes could be as a result of mud type used for drilling the wells.

## Remedy for contaminated soil

Different treatment techniques for soil are proposed for its remediation. These include treatment comprising of solidification/stabilisation and bioremediation.

### Treatment by solidification/stabilisation

Polluted soil can be excavated and mixed with fly ash, pulverized fuel ash (PFA) and Portland cement to create concrete like material, which then may be used (Amatya et al., 2002). These techniques are designed to accomplish;

- i) Reduction of pollutant solubility.
- (ii) Production of solid from liquid or semi-solid waste.
- (iii) Decrease in the exposed surface area across which transfer of pollutant chemicals may occur.

Solidification involves encapsulation of fine waste particles (micro encapsulation) or large blocks of waste (macro encapsulation) while stabilisation refers to the process of reducing the hazardous potential of waste materials by converting pollutants into their least soluble, mobile forms.

### Bioremediation

This involves the use of naturally occurring micro organism (in contrast to genetically engineered micro organism) to degrade and detoxify hazardous constituent (heavy metals) in soil to protect public health and environment, this technology involves spreading excavated polluted soils in a thin layer on the ground surface and stimulating aerobic microbial activity within the soils through aeration and/or the addition of minerals, nutrients and moisture.

The second process of soil treatment is by prepared bed reactors. In this system, the polluted soils are physically moved from original site to a newly prepared area which has been designed to enhance remediation and prevent transport of pollutants from site. Prepared bed reactors are designed in such a way that clay or plastic liners are placed underneath to retard transport of contaminants from the site.

## Remedy for contaminated water

Water treatment methods are varied, these ranges from sedimentation and clarification, distillation, coagulation and flocculation, carbon adsorption, reversed osmosis and so on. Suitable method like coagulation and flocculation or carbon adsorption could be employed to remove the wanton pollutant from the water before use.

## Conclusion

From the results of this study, it is evident that exploration and production activities introduced lots of heavy metals into the soil and groundwater where such activities are carried out. This has been traced to the many chemicals used for these activities. It is therefore suggested that remediation process be carried out so as to render the polluted soil and groundwater fit for use especially for agricultural and domestic purposes.

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