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The Physiochemical Indices of Soil Contaminated with Hydrocarbon and Heavy Metals in Petroleum Hydrocarbon Spilled Areas of Bodo and Bomu in Rivers State

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ABSTRACT
The present study was to determine the physiochemical indices of the soil contaminated with hydrocarbon and heavy metals in an oil spilled areas of Gokana local government area of Rivers State. Soil samples collected from two locations each of Apiapum in obubra local government area of cross River state(control) and Bodo/bomu in Gokana local government are of Rivers State, measured 1km by 1km. were selected randomly. The samples were bulked, digested and cleaned. Methods were developed for GC/FID and ICP-OES for hydrocarbon and heavy metals respectively. Equally, physiochemical indices of the soils were analysed in line with standard scientific procedures. Statistical analyses was done using mean, standard deviation percentage and analysis of variance. Results of the study revealed significantly ($p \leq 0.05$) higher concentration hydrocarbon (8,534.92±528.03mg/kg) in the contaminated soil than uncontaminated soil (0.00±0.00mg/kg). Correspondently, general increase in all the heavy metal concentrations except Cd (1.05±0.03mg/kg), and iron (269.13±3.83mg/kg) in contaminated soil was observed. The study also recorded significantly ($p \leq 0.05$) higher concentrations of Ca^+, K^+, and Na^+ ions in the contaminated soil than uncontaminated soil. The findings of the study also showed significant higher values of pH(8.3±0.24),total carbon content(1.77±0.07%),organic matter(2.64±0.50%),clayey soil(22.0±2.50%) and silt soil(15.0±2.50%) in the contaminated soil than uncontaminated soil. However, higher values of total nitrogen (0.83±0.04%), electrical conductivity (207.00±44.13µS/cm), available phosphorus (0.68±0.07mg/kg), and moisture content (14.02±2.59%) were revealed in uncontaminated soil than contaminated soil. The study has shown that soil contaminated with hydrocarbon and heavy metal can easily affect the physiochemical properties of the soil.
Key words: Soil contaminated, hydrocarbon, heavy metals, oil spill, and physiochemical indices.

INTRODUCTION/LITERATURE:

There is unabated growing public apprehension over wide variety of toxic materials being constantly released adventently or intentionally with the environment. One such materials are petroleum hydrocarbons that are in volumes caused by accidents, spills, leakages of moribund pipes, urban inputs, transportations, industrial and commercial or domestic uses (Ou *et al,* 2004, Wang and Stout, 2007). The contamination site is not only the sink of their release but distances in several kilometres far from the sources of release, where they have considerable impacts on the soil (Onyeagba and Isu, 2006). When the concentration of the petroleum hydrocarbon is far above normal, such that they cause harm to the environment and its constituents, they become pollutants. Pollution of the natural environment like the soil is universal problem because of its effect on ecosystem (Akoto *et al,* 2008). The soil is described as the unconsolidated or superficial layer of the earth crust lying below aerial vegetation and undecomposed dead organic matter and extending down to the limit to which it affects plant growth about their surface (Naraganan, 2000). It is a heterogeneous mixture of organic and inorganic matters, water, air, gases and microorganisms (Bhatia, 2006). The soil is considered as a store house of minerals, reservoir of water and water, conserver of fertility, a producer of vegetation and home to wild life, livestock, micro-organisms, forms bases for terrestrial ecosystem and a have a link between atmosphere,

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geology and land use (Narayanan, 2009). Petroleum hydrocarbon pollution leads to deterioration of the soil structure, loss organic matter content, loss of minerals like potassium, sodium, phosphate and nitrate etc (Akubugwo *et al* 2003). It is also observed that where ever there is high pollution of petroleum hydrocarbon, heavy metals are evident (Akamgbo and Jidere, (2001) and Rasheed, (2003) reported that petroleum hydrocarbon spill leads to availability of micro elements.

Aim/Objectives of the Study

The main aim of the study is to investigate the physiochemical indices of the soil contaminated with hydrocarbon and heavy metals in oil spilled areas of Bodo and Bomu in Gokana local government area of Rivers State.

Specific Objectives

To determine the concentration (mg/kg) of hydrocarbon in the contaminated soil and uncontaminated soil. To determine the concentrations (mg/kg) of heavy metals in the contaminated and uncontaminated soils. To determine the physiochemical indices of the contaminated and uncontaminated soils.

MATERIALS AND METHODS

Materials

Beckman couller centrifuge machine (Canada), Calrius 690 gas chromatographed. (Perkin Elmer, UK), 200 induction couple plasmas – optical emission spectroscope (London, UK), magnetic stirrer (India), microwave digester (USA), ADIIO pH meter (Hangary), agate pestle, aluminium foil, 100ml and 200ml beakers, Bushi extraction machine, digestive tube, garden shovel, manual hammering hallow metal pipe, polythene bags, soil samples, $CaCl_2$ diphenylamine indicator, H_3PO_4, 0.5N Ferrous ammonia sulphate solution, Conc. H_2SO_4 1.0N $K_2Cr_2O_7$, amyl alcohol, ascorbic acid, 40% NaOH, NaF, 5% SDS, $KHPO_4$, 0.5M $NaHCO_3$, sodium hexa meta phosphate, and water.

Methods

Soil sample of 100g each from two locations, each of the control (Apiapum in Obubra local government area of Cross River State and the research area (Bodo and Bornu in Gokana local government area of River State) were collected from the depths of 0-10cm, 10cm and 20cm) with area measured 1km by 1km. The samples were put in polythene bags and taken the laboratory. In the laboratory, each soil sample was soaked in 200ml deionized water in a beaker overnight. Each soaked soil sample was mixed by using constant speed mixture (500 rpm). The complete mixed soil was sieved with micro sieve for 20minutes and kept for drying. Dried soil sample was pounded in an agate mortar and filtered with plastic vial. Soil sample was then digested with mixture of HNO_3 and HF solution for 45 minutes at 175°C in a microwave digester. The digested soil was there aftern filtered and put in 100ml volumetric flask and made to 10ml with deionized water. Hydrocarbon extraction was carried out by soxhlet method (ASTM, 2005). The metals extraction was done in line with procedure found in the literature (Mielke *et al*, 2004). Estimation of total hydrocarbon was done in line with USEPA method 418 (Schwarts *et al*, 2012). Determination of heavy metals

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in the soil was conducted in line with EPA method, Moisture contents were estimated by gravimetric method (ASS, 1997), organic matter estimated by dichromate acid oxidation method (Nelson and Summer, 1982). Total nitrogen in the one was determined line with Kjeldhel method (Bremmer, 1983) and available phosphorus estimated by molybdenum blue method (Olseh and Cole, 1982).

RESULTS

Table1.0: Concentration in (mg/kg) of Hydrocarbon in Uncontaminated (Control) and Contaminated soils.

Constituent	Uncontaminated soil (control)	Contaminated soil
TPH (mg/kg)	0.00± 0.00	*8,534.92± 528.03

* Significant difference value. Mean ± SD of triplicate of the samples

Table2.0: Concentrations (mg/kg) of Heavy Metals in Uncontaminated and Contaminated soils.

Type of soil	Heavy metal/concentrations (mg/kg)							
	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Uncontaminated soil	*1.49 ± 0.03	0.21 ±0.03	66.62 ± 2.69	*269.13 ±3.83	137.20 ±5.23	2.01 0.09	38.60 ±3.93	39.72 ±1.88
Contaminated soil	1.05 ± 0.11	*15.41 1.43	*153.0 22.41	226.72 24.56	*401.30 ± 71.46	4.80 ± 0.51	*68.72 ±0.58	*193.50 ±7.47

*Significant differences in values. Mean ±SD of triplicates of the sample

Table 3.0 Physiochemical Properties of Uncontaminated and Contaminated Soil.

Physiochemical parameters	Uncontaminated soil (control)	Contaminated soil Experimental sample
Ph	7.6 ± 0.9	*8.3 ± 0.24
Total Nitrogen (%)	0.83 ± 0.04	0.70 ± 0.05
total Carbon (%)	0.98 ± 0.01	*1.77 ± 0.07
% Organic matter (%)	± 0.08	*2.64 ± 0.50
Electrical conductivity (uS/cm)	* 207.0± 44.13	192.00 ± 14.66
Available phosphate(mg/kg)	0.68 ± 0.07	0.47 ± 0.01
Moisture content (%)	*14.02 ±2.59	4.90 + 0.40

* Significant Difference Value. Mean ± SD of Triplicate of the Sample

Table 2.0 Concentrations (ppm) of macro Elements in Contaminated and Uncontaminated Soils.

Macro element	Uncontaminated soil((ppm)	Contaminated soil (ppm)
Calcium	* 561.14 ± 86.05	780.25 ± 98.85
Magnesium	179.0 ± 11.83	202.63 ± 9.22
Potassium	*120.75 ± 15.0	163.88 ± 6.96
Sodium	* 83.10 ± 3.35	* 83.10 ± 3.35

*Significant Difference Value. Mean ± SD of Triplicate of the Samples

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Table 3.0 Concentrations (%) of Soil Texture in Contaminated and Uncontaminated Soils.

Soil texture	Uncontaminated soil (%)	Contaminated soil (%)
Clayey soil	20.00 ± 2.00	*22.00 ±2.50
Sandy soil	*64.30 ± 3.00	62.00± 5.00
Silt soil	12.00 ± 4.00	*15.00 ± 2.50

* Significant Difference Value. Mean ± SD of Triplicate of the Samples

DISCUSSION

In table 1.0, it was observed that the total petroleum hydrocarbon in the contaminated soil (8,534.92± 528.03mg/kg) was significantly ($p \leq 0.05$) higher than in uncontaminated soil (0.00 ±0.00mg/kg). In table 2.0, general increase in all the heavy metal concentrations was observed except Cd (1.05±0.03mg/Kg) and iron (269.13 ±3.83mg/Kg) in the contaminated soil. Akamgbo and Jidere, (2001) reported that oil spill leads to availability of micronutrients. However, significantly higher concentrations of Cr^+, Cu^+, Mn^+, Pb^+ and Zn^+ were recorded at ($P \leq 0.05$) in the contaminated soil than in uncontaminated soil. Table 3.0 above revealed higher values of pH (8.30±0.24), total carbon (1.77±0.07%), and total organic matter (2.64± %) in the contaminated soil than with uncontaminated soil (pH (7.6±0.90), total carbon (0.98±0.01%), and total organic matter (0.68±0.08%). The high pH value may have been due to oiling that discouraged leaching of the basic salts in the contaminated soil (Obire and Nwabate, 2002). Jobson *et al*, (1974) opined that high organic matter in contaminated soil is due to the effect of hydrocarbon oil filing the pore spaces in the soil thus denying microbes of oxygen, which led to low decomposition of organic matter. Also, Osuji and Onajake (2006) attributed this to the metabolic processes following oil spillage that facilitates the addition of organic carbon from petroleum carbon by reducing the carbon mineralization capacity of micro flora. Conversely, higher values of soil moisture (14.02%), electrical conductivity (207.00±44.13μS/lcm), available phosphorus (0.68±0.07mglkg) and total Nitrogen (0.83±0.04%) were observed in uncontaminated soil than contaminated soil (4.90±0.00%, 192.00±14.66μS/cm, 0.47±0.01mg/Kg, 0.70±0.05%) for moisture content, electrical conductivity, available phosphorus and total nitrogen respectively (Table 3.0). Higher phosphorus content could be attributed to higher acidity which causes fixation of available phosphorus (Nnaji *et al*, 2002). The low nitrogen content in the contaminated soil could be due to imbalance in carbon to nitrogen ratio, and loss of nitrogen by hydrocarbon which retards growth of bacteria and use of carbons (Ayotamunu *et al*, 2006). The low electrical conductivity in contaminated soil could have been caused by sandiness which confers macro porosity (Mbagwu *et al*, 1983). The increase level in total Nitrogen content in uncontaminated soil sample could be due to the activities of nitrogen fixing bacteria and other microbes associated with decomposition of organic matter. Significant differences ($p \leq 0.05$) were observed in pH, total carbon, and organic matter, and electrical conductivity, available phosphorus between uncontaminated and contaminated soils. The results in table 4.0 also revealed that the concentrations of sodium (123.94±10.80ppm) potassium (163.88±6.96ppm), magnesium (202.63±9.22ppm) and calcium (780.25± 98.85ppm) were significantly ($p \geq 0.05$) higher in the contaminated soil than uncontaminated soil (83.10± 3.35ppm), (120.75±15.0ppm), (179.0± 11.83ppm) and (561.14± 86.05ppm) for sodium, potassium, magnesium and calcium respectively. This results disagreed with the opinion Akubugwo *et al*, (2003) BUT corresponded to the observation by Grusak, (2001). In table 5.0, it was observed that the percentages of clayey soil (22.0± 2.50%) and salt soil (15.0± 2.50%) in contaminated soils were significantly higher than in uncontaminated soil. (20.0±2.00%) and 12.00± 4.0%) for clayey and silt soils respectively. However, the percentage of sandy soil (64.00± 3.00%) was significantly higher in uncontaminated soil than contaminated soil at ($p \leq 0.05$). Xiao *et al*, (2014) reported that PAH strongly build up to the soil organic matter. The slight differences in particle size distribution was attributed to filtration rate of moisture content and drainage of soil (FAO, 1986).

CONCLUSION

The study has shown that in any environment that petroleum hydrocarbon is spilled, significantly high concentration of it finds full expression in the soil as well as heavy metals as an immediate sink. The presence of petroleum hydrocarbon and the corresponding heavy metals in the soil greatly determined the physiochemical indices of the soil. Examination of the physiochemical parameters of the soil is therefore essential in determining the type of remediation technology to be applied in restoring contaminated soil back to its original state.

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