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# **Evaluation of Heavy Metals and Physicochemical Parameters of Oil-contaminated Soil and Water Samples from Bonny, South-South, Nigeria**

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# *Authors' contributions*

*This work was carried out in collaboration among all authors. Author NCDU designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors EUE and COA managed the analyses of the study. Author COA managed the literature searches. All authors read and approved the final manuscript.*

#### *Article Information*

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# **ABSTRACT**

This study analyzed physical, chemical and selected heavy metals concentration of oil-polluted soil and water samples from Bonny, South-South, Nigeria. Unpolluted soil and water samples were used as controls. The pH of the test soil sample was acidic (4.24±0.03) when compared with control (7.6±0.05). Chloride, Phosphorus, Magnesium and Potassium concentrations of the test soil samples were 1151.614±0.37 mg/g, 1.23±0.02 mg/g, 11.27±0.34 mg/g and 11.52±0.5 mg/g respectively. Selected heavy metals such as Iron (Fe), Cadmium (Cd), Mercury (Hg), Arsenic (As), Lead (Pb) and Copper (Cu) showed that Hg and As were below detectable limits in test and control samples while Cd and Pb were below detectable limit in the control sample while test sample had 0.015±0.01 mg/g and 1.73±0.04 mg/g respectively. Fe and Cu contents were high at 38.7±0.13 mg/g and 5.49±0.05 mg/g when compared with the control at 3.52±0.02 mg/g and 1.08±0.03 mg/g. Total Petroleum Hydrocarbon (TPH), Total Organic Carbon (TOC) and Total Organic Matter (TOM) were at 5.93±0.13 mg/g, 3.64±0.1 mg/g and 4.23±0.1 mg/g respectively. Water pH, Temperature,

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Conductance, Dissolved Oxygen, Biological Oxygen Demand (BOD<sub>5</sub>) and Turbidity were 5.21±0.03, 25.1±0.01ºC, 610±0.04 µS/cm, 5.0±0.03 mg/l, 1.8±0.02 mg/l, and 53.50±0.06 NTU respectively. Chloride, Phosphorus, Magnesium, Potassium, Calcium and Bicarbonate concentrations of the water were 609.82±0.37 mg/ml, 1.03±0.02 mg/ml, 13.41±0.42 mg/ml, 7.68±0.3 mg/ml, 21.22±0.12 mg/ml and 4.3±0.07 mg/ml in that order. Arsenic and Mercury were below detectable limit in both test and control samples while Fe, Cd, Pb, and Cu were 42.2±0.6 mg/ml, 0.016±0.001 mg/ml, 1.9±0.04 mg/ml and 5.2±0.03 mg/ml respectively. Total Petroleum Hydrocarbon, Total Suspended Solids, Total Dissolved Solids, and Total Solids were 3.87±0.11 mg/ml, 23036±0.51 mg/ml, 396.5±0.3 mg/ml and 23433±0.4 respectively. The levels of detected heavy metals were higher than the World Health Organization (WHO) permissible limits and Nigerian standard set by Federal Environmental Protection Agency (FEPA). This indicates a moderate level of pollution in both soil and water samples, as a result, poses a serious threat to ecological and species survivability as well as growth and reproduction of aquatic and plant life.

*Keywords: Physicochemical; River Niger; tributary; heavy metals.*

# **1. INTRODUCTION**

Human activities which may be industrial or agricultural are the major cause of environmental pollution varieties of pollutants (wastes) which are indiscriminately discharged into the environment [1]. Rapid population growth, urbanization and industrialization and poor sanitary conditions among rural dwellers are the contributing factors of environmental pollution [2]. Waste generated from industrial, human and anthropogenic activities are either useful or hazardous to plants, animals and human beings (The end-user).

The soil which is a natural sink for various pollutants is naturally made up of varieties of minerals, organic constituents and broken rocks which are altered by environmental reactions. (Edori and Iyama, 2017). Pollutants that find their way into the soil interacts and changes the chemical and physical properties of the soil.

Soil has a limited capacity to contain pollutants. However, when such threshold is exceeded, the soil's ability to remove impurities, destroy disease-causing agents (pathogens) and degrade contaminants may be lost. The soil provides plant's physical support, air, water, temperature moderation, nutrients and protection from toxins. It also absorbs oxygen and methane and releases carbon dioxide and nitrous oxide. It also aids the conversion of dead organic matter into nutrients for plants and animals. Environmental pollution alters the soil's ability to perform optimally thereby leading to soil pollution [3].

Water as an essential component of life on earth contains minerals that are extremely important in human nutrition [4]. Human activities are a major factor determining the quality of surface and underground water. Through atmospheric pollution, effluent discharges, oil exploration, use of agricultural chemicals and eroded soils into water bodies, water loses its purity [5]. The level of physic-chemical parameters of water will determine the purpose with which the water could be best used for with little or no treatments. Variability in physicochemical parameters is responsible for the distribution of organisms in different freshwater habitat according to their adaptation, which allows them to survive in a specific habitat [6]. Major shifts in the stream bed composition and processes can alter species distribution, productivity and even change the production of greenhouse gases [7]. Temperature, dissolved oxygen (DO), carbon (iv) dioxide (CO<sub>2</sub>), pH, conductivity, Total Dissolved Solids (TDS), transparency and current among others and their regular and irregular fluctuations in water have been identified as determinants in river ecology (Blaber, 2000). It is, therefore, the aim of this research to evaluate heavy metals and physicochemical parameters of oilcontaminated soil and river tributary from Bonny, South-South, Nigeria.

# **2. MATERIALS AND METHODS**

#### **2.1 Study Area and Sample Collection**

Bonny River, an arm of the Niger River, is located in Rivers State, Southern Nigeria. It is one of the major and most important rivers in Rivers State. Bonny Island is approximately 40 km south of Port Harcourt in the Rivers State of Nigeria and on the eastward side of the Cameroon Mountain. The island lies on longitude: 7º00' and 7º15 E and latitude: 4º25'

and 4º50'N [8]. Soil samples were collected at a depth of 0–15 cm using sterile trowel after clearing debris from the soil surface. Samples for chemical analyses were collected in polyethylene bags, while those for microbiological analysis were collected in sterile screw-capped bottles. Analysis commenced immediately upon arrival in the laboratory [9].

Water samples were collected using sterile glass beakers into sterile sampling bottles. The samples were properly labeled and taken to the laboratory in an icebox for analysis [10].

#### **2.2 Chemical Analysis of Soil Samples**

#### **2.2.1 pH and conductivity determination**

The Physico-chemical properties of the soils were determined by using standard methods. The pH of the sample was determined using a Jewniary digital pH meter. Conductivity was determined using the CD303 conductivity meter.

Total Organic Carbon (TOC) was determined by the Walkley-Black dichromate wet oxidation method and the content of available phosphorus was determined using the method reported by Awe et al*.* [11]. Total Petroleum Hydrocarbon of Soil was determined by the method described by Eniola et al. [12] Heavy metal analysis was done wet digestion method on Atomic Absorption Spectra (AAS) [13].

#### **2.2.2 Physico-chemical analysis of water**

Water samples were analyzed according to standard methods [14] for physicochemical parameters such as pH, dissolved oxygen (DO), biological oxygen demand (BOD), phosphorus,<br>chloride, electrical conductivity (EC) and chloride, electrical conductivity Temperature. Total Solids, Total Dissolved Solids, Determination of Total Suspended Solids were determined by the method as reported by Ibrahim et al. [15].

#### **3. RESULTS AND DISCUSSION**

## **3.1 Mean Soil Chemical Parameters**

The results obtained in the soil analysis as shown in Table 1 indicates that the soil contains relatively high hydrogen ion concentration  $(H<sup>+</sup>)$ with a pH of 4.24±0.03 as compared with the soil control experiment that recorded a pH value of 7.6±0.05. The total petroleum hydrocarbon of polluted soil sample was higher than control with 5.93±0.13 mg/g and 0.34±0.01 for control. Total Organic Carbon and Total Organic Matter were higher in the polluted soil sample with values of 3.64±0.1 mg/g and 4.23±0.1 mg/g respectively.

#### **3.2 Soil Chemical Parameters**

Results obtained from the soil analysis showed that the soil contains relatively high hydrogen ion concentration (H+) with a pH of 4.24±0.03 showing an acidic range profiling on pH scale. The low pH range of the contaminated water and soil can be attributed to the nature of the chemicals in the soil such as polycyclic aromatic hydrocarbons (PAHS) e.g pyrene, naphthalene, etc that contain relatively high acidic contents. These components integrate itself into the soil and surrounding environment such as water and increase the hydrogen ion concentration of the medium. Chloride is an essential micronutrient that regulates enzyme activities in the cytoplasm, is a co-factor in photosynthesis, acts as a counter anion to stabilize membrane potential, and is involved in turgor and pH regulation [16]. According to Mahmood and Mansour [17]. Some non-biochemical roles of chloride (for example, osmotic regulation) need higher concentrations of this element. Unlike other micronutrients, chloride is not toxic when it accumulates to high levels in plants. The symptoms of chloride toxicity (higher concentrations) are associated with the osmotic effect of saline soils. Chloride toxicity is also associated with the activity of the nitrate reductase as nitrate and chloride have similar ionic properties and absorption mechanisms. When chloride uptake rises to the toxic level, it is easily converted to toxic compounds (like hypochlorites), before it can be detoxified with the nitrate reductase.

Total Petroleum Hydrocarbons (TPH) is a term used to describe a broad family of several hundred chemical compounds that originally come from crude oil. In this sense, TPH is a mixture of chemicals. They are called hydrocarbons because almost all of them are made entirely from hydrogen and carbon. Crude oils can vary in how much of each chemical they contain, and so can the petroleum products that are made from crude oils. TPH released to the soil may move through the soil to the groundwater. Individual compounds may then separate from the original mixture, depending on the chemical properties of the compound. Some

of these compounds will evaporate into the air and others will dissolve into the groundwater and move away from the release area. Other compounds will attach to particles in the soil and may stay in the soil for a long period, while others will be broken down by organisms found in the soil. Some authors [18,19] maintain that the rate of TPH degradation in the soil is primarily associated with the quantity and type of crude oil or drilling fluids, organic matter content and soil mechanical composition, soil moisture status and soil use as well as with the season in which increased TPH content was detected in soil.

Total organic carbon influences many soil characteristics including colour, nutrient holding capacity (cation and anion exchange capacity), nutrient turnover and stability, which in turn influence water relations, aeration and workability. TOC may also refer to the amount of organic carbon in the soil, or in a geological formation, particularly the source rock for a petroleum play [20].

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### **3.3 Heavy Metals Concentrations of the Soil**

Analysis of some heavy metals (Fig. 1) such as iron, cadmium, mercury, arsenic, lead and copper contents of the polluted soil sample showed that cadmium, mercury, arsenic and lead were below detectable limits in the control sample while mercury and arsenic were below detectable limits in the polluted soil. Iron, cadmium, lead, and copper were 38.7±0.13 mg/g, 0.015±0.01 mg/g, 1.73±0.04 mg/g and 5.49±0.05 mg/g respectively in the polluted soil sample.

Heavy metals are elements that exhibit metallic properties such as ductility, malleability, conductivity, cation stability and ligand specificity. They are characterized by relatively high density and high relative atomic weight with an atomic number greater than 20 [21]. Heavy metals are considered one of the major sources of soil pollution. Heavy metal pollution of the soil is caused by various metals, especially Cu, Ni, Cd,

#### **Table 1. Mean soil chemical parameters**







**Fig. 1. Soil heavy metals concentration**

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Zn, Cr and Pb [22]. Heavy metal pollution not only results in adverse effects on various parameters relating to plant quality and yield but also cause changes in the size, composition, and activity of the microbial community [23]. The adverse effects of heavy metals on soil biological and biochemical properties are well documented. The soil properties i.e. organic matter, clay contents and pH have major influences on the extent of the effects of metals on biological and biochemical properties. Heavy metals indirectly affect soil enzymatic activities by shifting the microbial community which synthesizes enzymes. They exhibit toxic effects on soil biota by affecting key microbial processes and decrease the number and activity of soil microorganisms [24].

### **3.4 Soil Mineral Concentrations**

Results from the analysis of soil minerals (Fig. 2) revealed that calcium was highest in both test and control samples with values of 19.34±0.12 mg/g and 18.23±0.1 mg/g for test and control samples respectively. This was followed by potassium which recorded 11.52±0.5 mg/g and 7.22±0.2 mg/g for test and control respectively. Magnesium was 11.27±0.34 mg/g and 6.27±0.1 mg/g for test and control samples respectively. Minerals such as phosphorus and bicarbonate were 1.23±0.2 mg/g and 1.78 ±0.02 mg/g for phosphorus test and control samples respectively while 2.3±0.05 and 1.89±0.03 mg/g for test and control samples respectively for bicarbonate.

Soil minerals play a vital role in soil fertility since mineral surfaces serve as potential sites for nutrient storage. However, different types of soil minerals hold and retain differing amounts of nutrients. Therefore, it is helpful to know the types of minerals that make up your soil so that you can predict the degree to which the soil can retain and supply nutrients to plants. Phosphorus occurs in the form of phosphates with other elements. Different forms of phosphates that are complex are found in the soil, water, plants, animals and humans. Soils with inadequate phosphorus content, plants will suffer, growth of crops will be stunted, leaves may change colour to purple and there will be a delayed time to flowering and growth of new shoots. Excess phosphorus in soil can become a point source of pollution because the excess not utilized by plants is washed away by runoffs into ponds, lakes and rivers [25].

Magnesium one of the dominant exchangeable cations in most soils. Soil Mg concentrations are generally sufficient for optimal plant growth, but highly weathered and sandy soils may be Mg deficient due to leaching by heavy precipitation. Magnesium is essential in the production of chlorophyll which allows photosynthesis [26].



**Fig. 2. Soil mineral concentrations**





*BDL: Below detectable limit*

Calcium is one percent by weight of soils and is generally available but may be lower as it is soluble and can be leached. It is thus low in sandy and heavily leached soil or strongly acidic mineral soil. Calcium is supplied to the plant in the form of exchangeable ions and moderately soluble minerals. Calcium is more available on the soil colloids than is potassium because the common mineral calcite, CaCO<sub>3</sub>, is more soluble than potassium-bearing minerals. Calcium is considered a secondary plant nutrient. Only nitrogen and potassium are required in larger amounts by plants, It is an important constituent of cell walls and can only be supplied in the xylem sap. Thus, if the plant runs out of a supply of calcium, it cannot remobilize calcium from older tissues [26].

Potassium is an essential plant nutrient and is required in large amounts for proper growth and reproduction of plants. Potassium is considered second only to nitrogen, when it comes to nutrients needed by plants, and is commonly considered as the "quality nutrient."

It affects the plant shape, size, color, taste and other measurements attributed to healthy produce. While K does not become a part of the chemical structure of plants, it plays many important regulatory roles in development. It increases crop yield and improves quality. It is required for numerous plant growth processes such as enzyme activation, stomatal activity (water use) and photosynthesis [27].

#### **3.5 Mean Physicochemical Parameters of Bonny River**

The physicochemical parameters of Bonny River as shown in Table 2 showed a relatively low pH of 5.12±0.3 when compared to that of the uncontaminated control at a pH of 7.2±0.02. A temperature of 32.3±0.03ºC and 25.1±0.04ºC for control and test sample respectively. Dissolved Oxygen (DO) concentrations of the control and test samples were 9.4±0.01 and 5.0±0.03 respectively. Biological Oxygen Demand (BOD) was 0.34±0.01 and 1.8±0.02 for control and test sample respectively. Heavy metals such as mercury and arsenic were below detectable limits in both the control and test samples. Total petroleum hydrocarbon (TPH), total suspended solids (TSS), total dissolved solids (TDS) and total solids (TS) of the test sample were 3.87±0.11 mg/ml, 23036±0.51 mg/ml, 396.5±0.3 mg/ml and 23433±0.4 mg/ml respectively.

Elevated levels of chloride in water bodies may threaten the sustainability of ecological food sources, poses a risk to species survivability as well as growth and reproduction of aquatic habitats [28]. The concentrations of chloride were relatively high in the test soil and water sample than in the control samples.

Electrical conductance is the measure of a solution's ability to conduct electric current which is greatly dependent on the availability of ionic species [29]. High electrical conductivity value is an indication that inorganic ions are in abundance in the water body. Conductivity value of 433±0.04 µS/cm and 610±0.04 µS/cm were recorded for control and contaminated test sample respectively. The ability of electric current to pass through water is proportional to the ionic concentration of solutes present in the water [30].

Dissolved oxygen (DO) is indispensable for the continued existence of aquatic life; hence it serves as a key indicator of ecosystem condition. Low DO concentrations can lead to impaired fish development and maturation, increased fish mortality, and underwater habitat degradation. The DO of the contaminated water sample was

lower at 5.0±0.03 mg/l when compared to that of the control at 9.4±0.01 mg/l. According to Julian et al., (2018) DO concentrations are dependent on the generation of oxygen through photosynthesis and consumption by living organisms especially bacteria. The discharge of wastewater with high levels of BOD into water bodies can cause serious dissolved oxygen depletion and death of aquatic animals in the receiving water bodies. The BOD value of the water was taken after five days of incubation and was 1.8±0.02 mg/l. this observed value significantly varied from the control water sample (unpolluted sample) which showed a BOD of 0.34 mg/l depicting much available dissolved oxygen for biochemical activities of inhabitants of the water. The concentration of solids indicates an important characteristic of water. Physical characteristics of water were determined based on solid concentration including total suspended solids (TSS) and total dissolved solids (TDS). Total dissolved solids (TDS), suspended solids (TSS) and total solids (TS) of the water were 396.5±0.3 mg/ml, 23036±0.51 mg/ml and 23433±0.4 mg/l respectively. These showed no significant variation from the control experiment which gave 392.0±0.3 mg/ml, 2300±0.5 mg/ml and 23431±0.42 mg/ml for TDS, TSS, and TS respectively. The higher concentration of TDS is due to the presence of dissolved inorganic and organic contaminants. When TPH is released directly to water through spills or leaks, certain TPH fractions will float in water and form thin surface films. Other heavier fractions will accumulate in the sediment at the bottom of the water, which may affect bottom-feeding fish and organisms. Some organisms found in the water (primarily bacteria and fungi) may break down some of the TPH fractions.

# **3.6 Heavy Metals Concentrations Water**

Fig. 3 reveals heavy metals concentrations of water. Cadmium, mercury, arsenic, and lead were all below detectable limits in the control sample. Mercury and arsenic were also below detectable limits in the test sample while cadmium and lead were 0.016±0.01 mg/g and 1.9±0.04 mg/g respectively in the test sample. Iron and copper were 42.2±0.6 mg/g and 5.2±0.05 mg/g respectively in the test sample while 12.2±0.13 mg/g, 1.08±0.03 mg/g respectively in the control sample.

Heavy metals are potentially toxic trace elements, and their impacts may be felt in organisms at low concentrations [31]. Heavy

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metals are not biodegradable, hence tend to bioaccumulate in aquatic organisms [32]. Heavy metals such as cadmium, mercury, nickel, zinc, chromium, and copper among others are toxic at high concentrations. The oral route has been detected as the main means through which heavy metals get into the human body system. People who fed on-farm produce irrigated with untreated and partially treated wastewater are prone to various ailments which effect might not be immediate [33]. Heavy metals are easily absorbed by aquatic life forms and accumulation may occur in higher concentration than in parent water bodies [34,35]. Fish can take up heavy metals either in their diets or through their gills [36] and bio-accumulate them at different rates in their muscles and organs [37]. According to Rainbow et al. (1980), the rate of accumulation and the ability to detoxify particular metals differ greatly. This may account for the variation in the concentration of heavy metals found in the different streams investigated in this study. Contamination of a river with heavy metals may cause devastating effects on the ecological balance of the aquatic environment, and the diversity of aquatic organisms becomes limited with the extent of contamination [38]. Cadmium (Cd) is a well known heavy metal toxicant with a specific gravity 8.65 times greater than water. The target organs for Cd toxicity have been identified as liver, placenta, kidneys, lungs, brain, and bones [39]. Lead (Pb) is physiological and neurological toxic to humans. Acute Pb poisoning may result in a dysfunction in the kidney, reproduction system, liver, and brain resulting in sickness and death. Copper (Cu) is an essential element in mammalian nutrition as a component of metalloenzymes in which it acts as an electron donor or acceptor. Conversely, exposure to high levels of Cu can result in several adverse health effects [40].

#### **3.7 Mineral Concentration of Water**

Fig. 4 shows the concentration of minerals in the water. Phosphorus recorded the least concentration of mineral with 1.03±0.02 mg/g and 1.8±0.04 mg/g for test and control samples respectively. This was followed by bicarbonate and potassium with 4.3±0.07 mg/g and 1.89±0.03 mg/g for test and control sample in that order for bicarbonate while 7.68±0.3 mg/g and 4.22±0.2 mg/g for test and control samples respectively for potassium. Mineral concentration was highest in calcium with 21.22±0.12 mg/g and 20.23±0.1 mg/g for test and control samples respectively. This was followed by magnesium

which recorded 13.44±0.42 mg/g and 8.27 ±0.2 mg/g for test and control samples respectively.

Though phosphorus promotes plant growth in soils, yet its excess in water promotes algal growth, which if persistently continues can lead to an algal bloom. Algal bloom leads to oxygen deficiency in water with the consequence of the death of aquatic animals and odour. The amount of total phosphorus indicates the degree of water pollution, i.e., the presence of faecal wastewater,

chemical fertilizers and detergents (surfactants). Calcium and magnesium are very common elements. Calcium is the fifth most abundant natural element and magnesium the eighth. Both elements are present in all natural waters. The most common source of calcium and magnesium in groundwater is through the erosion of rocks, such as limestone and dolomite, and minerals, such as calcite and magnesite. Sources of these elements in groundwater from the area calcite and magnesite and are the major contributors to



**Fig. 3. Heavy metals concentrations of water**



**Fig. 4. The concentration of minerals in water**



#### **Table 3. Comparing samples with standards**

*BDL: Below detectable limit. NS: Not Specified*

the hardness of the water, though hard water is not a health hazard, but it can be a nuisance in homes. One other importance of calcium in groundwater, for example, is its ability to block the absorption of heavy metals in the body and is thought to increase bone mass and prevent certain types of cancer. Magnesium in drinking water may have a laxative effect. However, the human body tends to adapt to this laxative effect with time [41].

Table 3 compared the water test sample with the World Health Organization standard (WHO) and Nigerian standard set by the Federal Environmental Protection Agency (FEPA).

Result obtained showed that the pH, BOD and TDS were below WHO and FEPA permissible limits. Turbidity, chloride, iron, lead, copper, and TSS were all above WHO and FEPA permissible limits. Water temperature was above WHO permissible limit and below the FEPA limit. Phosphorus was above WHO permissible limit and within the limit set by FEPA. Conductivity was above the FEPA standard and below the WHO permissible limit. Cadmium was within WHO permissible limit and below the FEPA standard.

### **4. CONCLUSION**

This study revealed that the soil and water samples were acidic as a result of oil pollution,

this poses a serious threat to ecological and species survivability as well as growth and reproduction of aquatic organisms and plant life. The soil could be said to be infertile for agricultural purposes and discourages support for the fecundity of both plants and animal species.

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#### **COMPETING INTERESTS**

Authors have declared that no competing interests exist.

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