

Characterization of Environmental Samples around an Indigenous Refinery in Nigeria

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Abstract: Co-contamination by petrochemicals and heavy metals emanating from refinery operations was investigated from sludge, soil and water samples immediately around WRPC refinery, Delta State, Nigeria. Collection and assessment of environmental samples from 5 different points across the refinery and groundwater for which the pH, Electrical Conductivity, Temperature, Turbidity, TDS, TSS, Total hardness, Alkalinity, DO, BOD, Cl^- , PO_4^{3-} and bacteriological analysis were measured. The total petroleum hydrocarbon and polycyclic aromatic hydrocarbon concentrations were 755.291 and 22.746 mg L^{-1} in the water samples, 8756.148 and 311.569 mg kg^{-1} for the soil samples, 65346.8 and 4190.598 mg kg^{-1} for the sludge samples via GC-MS analysis. The effects of the release of the industrial effluents caused the increase in pH, 5.2-5.3 across the studied samples. Conductivity measurements for the sludge, soil and water samples gave readings of 0.27, 0.25 and 0.48 $\mu\text{S cm}^{-1}$ respectively. The presence and distribution of different heavy metals varied whereby the presence of cadmium (0.139 mg/l), cobalt (0.34 mg/l) and nickel (0.606 mg/l) in the water samples were above the WHO permissible limits. The highest concentrations of iron (108.77 mg/kg) and zinc (11.072 mg/kg) were observed in the soil samples while chromium (24.25 mg/kg), lead (3.902 mg/kg), mercury (0.21 mg/kg), arsenic (0.417 mg/kg), copper (2.015 mg/kg) and manganese (82.695 mg/kg) were highest in the sludge samples. Total bacterial enumeration revealed a count of 7.29×10^3 (cfu/g), 1.84×10^3 (cfu/g) and 1.32×10^3 (cfu/ml) in the soil, sludge and water samples respectively. The presence and concentrations of these mixed pollutants via the activities of the refinery resulted in change of known physicochemical properties which in turn affects the vegetative and microbial flora within the area.

Keywords: Total Petroleum Hydrocarbons, Polycyclic Aromatic Hydrocarbons, Heavy Metals, Physicochemical Properties

1. Introduction

The persistent use of petroleum and the increased demand for its by-products for numerous applications places a huge constraint on the immediate environment [1-2]. Operational activities around petroleum refineries like several in the Niger Delta region of Nigeria are renowned for its cumulative oil spills due to large oil deposits [3-5]. These sites are poorly and most often never investigated to know the extent of petroleum hydrocarbon contamination and as a result there is high possibility of accumulation of these pollutants in the food chain by their consumption in drinking

water, fish and crops, which could pose a risk to human and other terrestrial and aquatic life [6-8]. Crude oil pollution from spills and poor waste disposal affect the physicochemical properties of soils with sometimes also the build-up of high concentrations of heavy metals in the affected sites [9]. Overall, the sources of livelihood in impacted areas which include farmlands, rivers and forests have been negatively affected [10].

Polycyclic aromatic hydrocarbons (PAH) and BTEX (benzene, toluene, ethylbenzene and xylene) represent uniquely hazardous components of petroleum hydrocarbons [11-13]. Exposure to such compounds for prolonged periods

can cause the distortions of soil texture, saturated hydraulic conductivity, porosity and compaction in addition to creating a generally unsuitable environment for the growth of biological life [14-15].

Co-contamination by inorganic compounds like heavy metals, radionuclides and other synthetic compounds, all constitute the main mix of environmental pollutants around petrochemical industrial areas [16]. Although heavy metals at extreme concentrations are toxic to microorganisms, plants, animals and humans, a substantial proportion of minerals (metals at acceptable concentrations) are beneficial [17]. Within the sludge, a number of factors influence heavy metal use in sludge, such as pH, redox potential, the presence of other ions, organic matter content, sludge texture, microbial activity, etc. The toxicity of different forms of heavy metals depends on factors such as physical state, gas, solution, or powder particle size, cell adsorption rate, elimination rate, and the nature of chemical substituents in the toxic compound [18].

Quantification of the respective types and concentration of polluting agents creates a necessary baseline for the protection and remediation of the immediate environment around petrochemical industries. Studies show that preliminary tests geared towards the soil and water physical, chemical and biological characteristics underlines the success of remediation strategies that could be employed as well as serves as the basic indicators to monitor soil pollution [19-20]. The aim of this study was to assess the effect of petroleum hydrocarbons on the physicochemical properties of sludge, soil and water from an indigenous oil refinery, Warri Refinery and Petrochemical Company (WRPC) Ltd.

2. Materials and Methods

2.1. Sample Collection

US EPA (SW-846) guidelines were applied, using simple random sampling for collecting oily sludge/sediment samples. A total of fifteen (15) samples were used for the present analysis. Five (5) oily sludge samples were randomly collected with core sampler in a 500 mL wide-mouth glass jar from the project site area of Ubeji (an area bounding WRPC, and popularly referred to in this study as WRPC Phase 2 Clean-up project). Five (5) soil samples were randomly collected using soil auger from the oil-impacted environs and stored in sealed polythene bags. The subsamples were homogenized to get a composite sample of each and were properly labelled and transported to the laboratory for pre-treatment and analyses. The soil samples were air-dried for two weeks, rolled manually, mixed and sieved with 2 mm mesh to remove stones and debris. Also, five (5) water samples were collected in the said area in well-labelled 1-liter amber glass bottles with teflon-lined screw cap and were preserved at the time of collection with concentrated HCl to pH < 2 and held at 4°C immediately after collection until extracted within 14 days.

2.2. Hydrocarbon Analysis

The liquid-liquid extraction (LLE) technique as stated in the USEPA Method 3510 was employed in conjunction with Method 3500c for the water sample. 1 liter of the sample was serially extracted with 60 mL of methylene chloride at a pH greater than 11 (with sodium hydroxide solution) and again at a pH less than 2 (with sulfuric acid) using a separatory funnel with the intent of achieving good recovery of the desired analytes. 1.0 mL of the surrogate spiking solution was added and mixed. The technique required strong shaking with periodic venting to release excess pressure, followed by the separation of the organic layer (extract) from the aqueous phase. The extract was then filtered through a desiccant (anhydrous Na₂SO₄) to remove moisture and concentrated using Snyder column to a volume of 1 mL prior to the analysis. A test portion of 5.00g of the soil sample was weighed into 20-mL glass scintillation vials, and 10 mL of methylene chloride was added to each vial. The vials were sealed with a foil-lined cap and shaken on a reciprocating platform shaker (Eberbach 6010, Fisher Scientific, St. Louis, MO) at 120 cycles/min for 1 h. The extracts were centrifuged for 10 min at 2000 rpm and removed carefully from the centrifuge, and the extraction solution was decanted and stored at 4°C until analysis. For the oily sludge sample, soxhlet extraction (EPA Method SW-846 3540) was employed because it is quite efficient for the extraction of the semivolatiles. 20 g of sample was extracted using 500 ml of methylene chloride for 24 h. 10 g of anhydrous sodium sulphate was mixed with the sample immediately prior to extraction to remove water.

Replication of extraction ranged from n=3 to n=5. The extraction solutions were sealed in glass vials and stored at 4°C until analysis. All the samples were analysed by GC/MS using an Agilent 7890 Series GC (Agilent J&W DB-UI 8270D) coupled with MS 6975 MSD single quadrupole system. Analysis of total petroleum hydrocarbons (TPH) and quantification of polyaromatic hydrocarbons (PAHs) in each sample was performed according to EPA method 8270D-2007 [26-27].

GC-MS Instrumentation and Conditions

GC-MS analysis was performed on an Agilent 7890 Series GC (Agilent J&W DB-UI 8270D) coupled with MS 6975 MSD and a 30 m, 0.32 mm ID 0.5µm film thickness fused silica capillary column. Helium was used as the carrier gas and the column head pressure was maintained at 10 psi to give a flow rate of 1.0 ml/min. The injector and transfer line were set at 270°C and 320°C, respectively. The initial temperature was kept at 80°C for 1 min, ramped to 200°C at a rate of 5°C/min, to 270°C at 3°C/min, and ramped to 320°C at 15°C/min and held at that temperature for 10 min. A 1µg/L aliquot was injected in the splitless mode with a 1-min purge-off. The MS was scanned from 50 to 550 amu range at 0.8 scan/s by selecting full-scan mode. The quantification of TPH in a sample from the GC run was conducted through total chromatographic area counts based on internal standards (IS). HP MS-ChemStation (DOS series) was used to program

the data acquisition and analysis.

2.3. Determination of Soil Physicochemical Properties

Percentage moisture content was determined using standard methods [21]. 1kg each of soil and sludge samples were weighed out and heated overnight at 105°C in an oven. The samples were then allowed to cool for an hour in a desiccator prior to taking weight measurements. The percentage moisture content (% MC) was calculated using the equation below;

$$\% MC = \frac{[\text{Weight of wet soil (g)} - \text{Weight of dried soil (g)}] \times 100\%}{\text{Weight of wet soil (g)}}$$

Sludge, soil and water pH analysis was determined for all samples using a digital pH meter (Jenway model 3015) with a glass-calomel electrode combination with vigorous stirring [22]. Approximately 10g each of soil and sludge samples were crushed, air-dried and sieved using a 2.0mm mesh then weighed into a 100ml beaker to which 20ml distilled water was added (ratio 1:2 soil/sludge to water). The suspensions were stirred vigorously with a glass rod to form homogenous slurries then left to stand at room temperature for 20 minutes. pH was determined using a pre-calibrated Jenway 3015 pH meter. Then the glass electrode of the pH meter was placed into the settled suspension in each beaker and the pH value of each sample beaker was recorded. Conductivity measurements were determined using a conductivity meter (Systronics-304) on a fresh soil, sludge and water samples at 25°C. The total organic matter was quantified according to standard methods [21]. Total alkalinity, sulphates and chlorides were estimated using standard protocols [23]. The temperature of all three samples was determined in-situ using the mercury-in-glass thermometer. Total hardness by titrimetric method, total dissolved solids by gravimetric methods, total suspended solids by filtration method, dissolved oxygen by titrimetric method, dissolved oxygen and biological oxygen demand by APHA method [24].

2.4. Estimation of Microbiological Population

Enumeration of the total bacterial count was determined using the most probable number (MPN) method by which heterotrophic bacteria was estimated using colony counts on nutrient agar via the pour plate technique [25].

2.5. Heavy Metals Analysis

5 g of each soil sample was digested using aqua regia digestion method (USEPA 3050). After filtration through a

funnel lined with Whatman No. 42 filter paper, the filtrate was collected into a 100 ml well-labeled polyethylene bottle prior to analysis. All digestions were carried out in triplicate for each sample and the amounts of trace metals recorded as mean value. 500 ml of each water sample was evaporated to about 100 ml, then, 10 ml of conc. HNO₃ was added and the solution was placed on a heating mantle at low heat for 30 min. After cooling, it was filtered and made up to 100 ml with deionized-distilled water. For the oily sludge sample, US EPA Method 3031 for acid digestion of oils for metals was applied with little adjustment. A representative 5.0 g sample of the oily sludge was mixed with 3.0 g of finely ground potassium permanganate and then 2.0 mL of concentrated H₂SO₄ was added while stirring. A strong exothermic reaction occurs. The sample was then treated with 2 mL concentrated HNO₃. 10 mL of concentrated HCl was added and the sample was heated until completion of reaction and then filtered. To remove the manganese, the digestate was neutralized with concentrated ammonium hydroxide. The sample was brought to volume. The extracts were analyzed for heavy metals (Cr, Cd, Pb, Ni, As, Cu, Co, Mn, Fe and Zn) using atomic absorption spectrophotometer (AAS) iCE 3000 Series at their respective wavelength (357.9, 228.8, 283.3, 422.7, 232.0, 324.8, 240.7, 279.5, 248.3 and 213.9 nm) according to APHA method [APHA, 2009]. Hg was analyzed by the flameless AAS using the cold vapour mode.

3. Results and Discussion

The numerous processes and facilities within the refinery, coupled with the procedure of handling as well as storage serve as avenues for release into the environment. In this study, the total petroleum hydrocarbon (TPH) and polycyclic aromatic hydrocarbon (PAH) concentrations in the sludge, soil and water were detected in each sample at 65,346.8 (mg/kg), 4,190.6 (mg/kg) in the sludge, 8,756.1 (mg/kg), 311.6 (mg/kg) in the soil and 755.3 (mg/l), 22.7 (mg/l) for the water samples respectively (Table 1).

Discharge from petrochemical industries, laced with a range of chemicals, trigger environmental and health concerns. Quantification of the soil, sludge and water surrounding the refinery in this study is an important physical factor in the determination of the toxicity levels which would otherwise contaminate the food chain by way of useful microorganisms, plants and marine organisms.

Table 1. Hydrocarbon concentration of samples.

Sample	Total Petroleum Hydrocarbon (TPH)	Total Polycyclic aromatic Hydrocarbon (TPAH)
Water sample	755.291 (mg/L)	22.746 (mg/L)
Sludge sample	65346.8(mg/kg)	4190.598(mg/kg)
Soil sample	8756.148(mg/kg)	311.569(mg/kg)

The pH of the environment is important as different vegetable and microbial life forms blossom at varying pH levels, usually tending to neutral [28]. It was, therefore, very

important to determine soil pH in this study. Data obtained showed that the pH of the studied samples were 5.2, 5.3 and 5.3 for the soil, sludge and water respectively (Table 2). The

pH range of oil contaminated environments general tends to be acidic with a reduced level of porosity as against the norm of 6.7 [29]. Run-offs from the refinery would account for the increased in pH observed in the sludge samples as the source of the concentrated pollutants whereby via the natural process of leaching, these contaminants leach out into the waterways resulting in the increased pH of the water samples.

This as well could dissipate the fundamental salts in the sludge and water samples with active movement in the soil as

the zone in between the point of origin and its final destination; the water ways.

As a physicochemical parameter, pH regulates the ion solubility and availability, thereby influencing plant and microbial activities and dispersion of nutrients [21].

Furthermore, the pH level is a good indicator of the polluting elements end-point, leachability and decomposition which in effect affects the physical, chemical and biological properties of the environment [28].

Table 2. Physicochemical parameters of oily samples.

Parameter	Sludge	Soil	Water
pH	5.3	5.2	5.3
Conductivity ($\mu\text{S}/\text{cm}$)	0.27	0.25	0.48
Temperature ($^{\circ}\text{C}$)	-	-	29.6
Moisture content (%)	3.70	1.00	-
Total hardness (mg/l)	-	-	145
Organic matter (%)	7.83	8.27	-
TDS (mg/l)	-	-	1576
Total alkalinity (mg/l)	0.82	1.05	0.65
TSS (mg/l)	-	-	1479
Sulphate (mg/l)	10.59	12.73	24.81
DO (mg/l)	-	-	1.83
BOD (mg/l)	-	-	194
Chloride (mg/l)	319	295	288
Oil and grease (mg/l)	15756	15628	975

The lower moisture content observed in the soil samples compared to that of the sludge is attributed to the presence of total petroleum and polycyclic aromatic hydrocarbons, which a study has reported causes an increase in soil hydrophobicity which would lead to a reduced moisture holding capacity [30]. Such contaminants trigger the release of carbon dioxide from the soil which in time would later affect the pH.

The presence of petroleum contaminants in environmental samples affects the concentration of ions via the availability of dissolved solutes. Electrical conductivity was significantly higher in the water samples thus confirming the absence of petroleum products or the presence of a much reduced concentration of contaminated oil and hydrocarbon by-products in the water samples (Table 2). Other researchers discovered that the dissolution of minerals particularly via natural degradation caused an increase in pH, electrical conductivity and total dissolved solids in water and soil samples [31]. Other factors considered to be directly impacting on the electrical conductivity of the environmental samples in this study would be the absence of oxygen, the presence of electron acceptors like nitrate ions and any possible dehydrogenation events taking place [21]. The lower levels of alkalinity in the sludge and water samples suggests that the inorganic elements, the macronutrients, within each sample reduces upon exposure to the polluting oils [32].

Organic matter is a characteristic feature of that affects the bioavailability of nutrients in an environmental sample and is closely related to both biodiversity population as well as the moisture content whereby a higher moisture content support the growth and availability of microorganisms which in turn supports plant metabolism via plant transport systems [33]. Organic matter is expected to be higher in petroleum contaminated environments as has been reported Ayodele

and Omotoso [34]. In this study, the values obtained in the sludge sample was high, 7.83% respectively which was within the reported range observed in another report [34]. The 8.27% organic matter content observed in the soil samples could be attributed to the presence of other organic additives like pesticides, fertilizers, in particular would be dead or decaying plant material. All natural water ways contain acceptable limits of dissolved solids and a mixture of suspended organic and inorganic substances [35]. The obtained value for the total dissolved solids (TDS) was 1576 (mg/L). Research show that electrical conductivity and total dissolved solids and soluble solids (TSS) share a linear relationship whereby the higher the electrical conductivity, the higher the TDS and total soluble solutes [36].

Enumeration of the bacterial population of the studied samples (Table 3) revealed that the soil sample possessed a higher quantity of microorganism per gram (7.29×10^3 cfu/g) in comparison to that of the sludge (1.84×10^3 cfu/g) whereas that of the water sample was 1.32×10^3 (cfu/ml). A higher concentration of microorganisms in the soil was expected as such are organism are ubiquitous in nature, existing in all habitat types.

Table 3. Bacteriological analysis results.

SAMPLE	TOTAL BACTERIAL COUNT (TBC)
Water sample	1.32×10^3 (cfu/ml)
Sludge sample	1.84×10^3 (cfu/g)
Soil sample	7.29×10^3 (cfu/g)

The augmentation of soil microorganisms with that obtained from the sludge would undoubtedly increase the microbial number particularly if such microorganisms already possess a form of tolerance to certain limits of

hydrocarbon bombardment. In this study, the enumerated bacterial numbers were not as high as other reported studies which suggests that the control limits for petroleum product within the soil had elapsed, thereby leading to a loss of viable organisms, as a result reducing their population [31], [37-40]. Other considerations include the cascading events triggered by the spill of excess hydrocarbons which increase the pH and causes a reduction in porosity as well as a disruption of

gaseous exchanges via the retention of carbon dioxide, the presence of petroleum additives like heavy metals, etc, all of which lead to a reduction in the population of microorganisms in the contaminated environment [41]. Heavy metals are useful for biological growth and development but when they are introduced via leach or chemical reactions from storage tanks, petroleum pipelines, etc [42].

Table 4. Heavy metals concentrations of the samples.

Heavy metals	Soil (mg/kg)	Sludge (mg/kg)	Water (mg/l)
Chromium	0.640	24.250	0.129
Cadmium	0.090	0.038	0.139
Lead	1.052	3.902	0.234
Mercury	0.136	0.210	0.032
Nickel	0.278	0.459	0.606
Arsenic	0.215	0.417	0.098
Copper	0.263	2.015	0.201
Cobalt	-	0.275	0.340
Manganese	10.082	82.695	31.467
Iron	108.771	94.721	47.304
Zinc	11.072	9.909	8.209

Data obtained in this current study (Table 4) revealed that with the exception of nickel, iron and zinc, the sludge samples contained the highest concentrations of chromium (24.25 mg/kg), lead (3.902 mg/kg), mercury (0.21 mg/kg), arsenic (0.417 mg/kg), copper (2.015 mg/kg) and manganese (82.695 mg/kg). These elements were expected to be detected in the sludge samples but in lower concentrations as part of industry awareness of their deleterious effects on the environment, thereby necessitating containment and treatment processes prior to release. In the immediate soil around the environment, iron (108.77 mg/kg) and zinc (11.072 mg/kg) where highest of all studied samples as these are already present in the soil, performing important metabolic functions to both vegetative and microbial life [42]. The higher concentrations of various heavy metals in soil samples is attributed to their release from industrial effluents. The higher presence of cadmium (0.139 mg/l), cobalt (0.34 mg/l) and nickel (0.606 mg/l) in the water samples are all above the permissible world health organization (WHO) limits for ground water [43]. Effluents from the petrochemical industrial activities would account for this and also serves as a measure to determine whether the treatment or containment facilities in place require an upgrade.

4. Conclusion

Data obtained in this study has shown that higher concentrations of TPH and TPAH were obtained from the sludge (65,326.8 and 4,190.598mg/kg) than that of the soil (8,756.148 and 311.569 mg/kg). The presence of these hydrocarbons contributed to the measured differences in the physicochemical characteristics of the samples which leaches into the waterways (755.291 and 22.746 mg/L) via the soil where it accumulates and enters the food chain (Table 1). This study showed that the elevated concentrations of

petroleum products and heavy metals, accumulate in the soil and water which affects their physicochemical properties, including microbial life (Table 2-4). The presence of these mixed concentration of pollutants causes an increase in soil pH, leaning towards acidic (5.2-5.3) in the soil, sludge and water samples in addition to a reduction in porosity, increased carbon dioxide presence and an increase in electrical conductivity all of which reduces the availability of essential nutrients in each environmental sample. The results of the study could be utilized as a baseline towards the development and implementation of both remediation and in situ containment techniques.

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