

Research Article

Spectra Analysis of Endocrine Related Compounds and Heavy Metals in Petroleum Hydrocarbon Impacted Soil

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Abstract

There has been increasing influx of noxious pollutants into the ecosystem, these recalcitrant affect all biosphere of life including human progression. Petroleum compounds are the chief source of hydrocarbons and their processing contributes to various fractions of potent poisons into the ecosystem. Petroleum hydrocarbon impacted soil was sampled from spilled sites located within the hinterlands of Rivers state Nigeria and using a spectroscopic assay method, they were examined for the presence of heavy metals and chemicals associated to bisphenol-A bioaccumulation. The collection point for the control experiment was roughly 1.04 kilometers away from the suburban city. The test and control studies revealed the presence of heavy metals Fe, Pb, and Cu, respectively. However, the concentrations of Fe and Pb were rather high, measuring 14.01 ± 0.05 and 3.52 ± 0.2 mg/ml, respectively. Cu was found at 3.22 ± 0.25 and 1.08 ± 0.45 mg/ml for the test and control experiment respectively while 4.56 ± 0.15 mg/g of Pb was identified in the test experiment only. Heavy metals of Cd, Ni, As, Pb and Mn were below detectable limit in both experiments, respectively. FTIR spectroscopy revealed that sample II's amide I was severely deformed, but all of the damaged soil samples had significant hydroxylation at about 3300 cm^{-1} . The impacted soil sample also exhibited evidence of amide I bending. Because of the population's increasing demand for elite supplies, there is a growing number of oil drilling and exploration businesses in our nation, making the current study of clinical and environmental health vital. The results of this assessment will serve as a suitable manual for monitoring organizations, enabling them to strictly enforce policies for exploration and tighten all departure ports in order to safeguard the ecosystem right away.

Keywords

Petroleum Hydrocarbon, Heavy Metals, Bisphenol-A, FTIR-Spectroscopy

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1. Introduction

Environmental impacts on soil are hence mainly attributed to the petroleum industries; this is because petroleum hydrocarbon impacted soil causes organic pollution of the local ground water. One of the major environmental problems we have today is hydrocarbon contamination giving rise to heavy metals and organic compound such as Bisphenol A resulting from the activities related to petrochemical industries. Crude oil, a complex hydrogen pollutant is made up of different mixtures of compounds [1, 2, 4, 6]. Petroleum hydrocarbons can be divided into four classes: Aromatics, Saturated, Asphaltenes (phenols, fatty acids, ketones, porphyrins and esters) and Resins (quinolones, carbazoles, amides, pyridines and sulfoxides); which are reported frequently as petroleum hydrocarbon impacted soil contaminants [2]. The communities which were exposed to hydrocarbons became adapted, exhibiting selective enrichment and genetic changes.

The primary energy source for daily living and the industrial sector is petroleum-based goods [8, 23, 27, 29]. Regular accidents and leaks happen when exploring for oil, extracting it, refining it, transporting it, and storing petroleum and petroleum products [12, 39, 45]. Hydrocarbon-contaminated soil severely harms regional ecosystems because contaminants build up in the tissues of plants and animals, sometimes leading to mutagenic or fatal outcomes. Concerns about worldwide public health, particularly in developing nations, have recently increased due to environmental contamination caused by high concentrations of organic chemicals and heavy [10]. According to Oparaji et al. [33] copper (Cu), zinc (Zn), cadmium (Cd), lead (Pb), arsenic (As), and mercury (Hg) are the main hazardous heavy metals that cause soil pollution. When organic contaminants are released into the environment, they are difficult to remove, unlike heavy metals, which eventually break down into carbon dioxide and water. Until they are released by modifications in the hydrogeology, weather patterns, or the abundance of plants, these metals remain in the environment after attaching to soils and sediments [20, 29]. Furthermore, organic substances like bisphenols and polycyclic aromatic hydrocarbons (PAHs), which are produced by burning or disposing of trash from homes, businesses, electronics, plastics, and medical applications, seem to find a home in polluted soils [25, 26]. These organic compounds exhibit excellent durability, poor mobility, and a strong affinity for soil organic materials in the soil. Additionally, it has been noted that contamination by heavy metals frequently coexists with contamination by other contaminants in dumpsites where solid wastes are burned [30, 38].

The chemical bisphenol A (BPA) is widely used in a variety of consumer goods, medical supplies, and drinking water in small amounts [31]. It is a significant industrial chemical

that is frequently employed as epoxy resin and polycarbonate plastic monomers [14, 5]. Everyday items that come into touch with food, like plastic bottles, cups, plates, goblets, and storage containers, often contain BPA.

Heavy metals which are natural substances in the Earth's crust, are widely spread in environment and foods. They defined as those elements having an atomic number greater than 20 and atomic density above 5gcm^{-3} and must exhibit the properties of a metal [13-18]. The heavy metals can be broadly classified into two categories: Essential and Non-essential heavy metals.

Existing knowledge and literature acknowledges the importance and necessity of quantification of heavy metals and Bisphenol A present in the petroleum contaminated soil, but a comprehensive investigation into the chemical composition and concentrations of these compounds is necessary for more understanding. The lack of detailed information hinders both the scientific progress and effective environmental management practices. This study is carried out to help bridge the gap by utilizing advanced analytical techniques to ascertain the specific heavy metals and bisphenolA present in soil samples impacted by petroleum hydrocarbon. Through this quantification analysis and the exploration of their spatial distribution, the research aims at providing an understanding of the environmental implications and hazards contamination by heavy metals and bisphenol A and ensuring the restoration of soil quality with the preservation of ecosystem health around the globe.

2. Materials and Methods

2.1. Materials

All the reagents, equipment used in the present study were of analytical grade and products of BDh, May and Baker, Sigma Alrich. The equipments are calibrated at each use.

2.2. Methods

Collection of the Experimental Samples

2.3. Soil Samples

Petroleum hydrocarbon contaminated soil was collected Agbada oil field (LONG. $7^{\circ} 00''$, $57^{\circ}.3''$ E; LAT. $4^{\circ} 53''$, $70^{\circ}.04''$ N) located at Portharcourt, Rivers state, Nigeria as described by Ezenwelu *et al.* [19]. The soil was collected in clean sterile sample containers and was taken to the lab for further experiments.

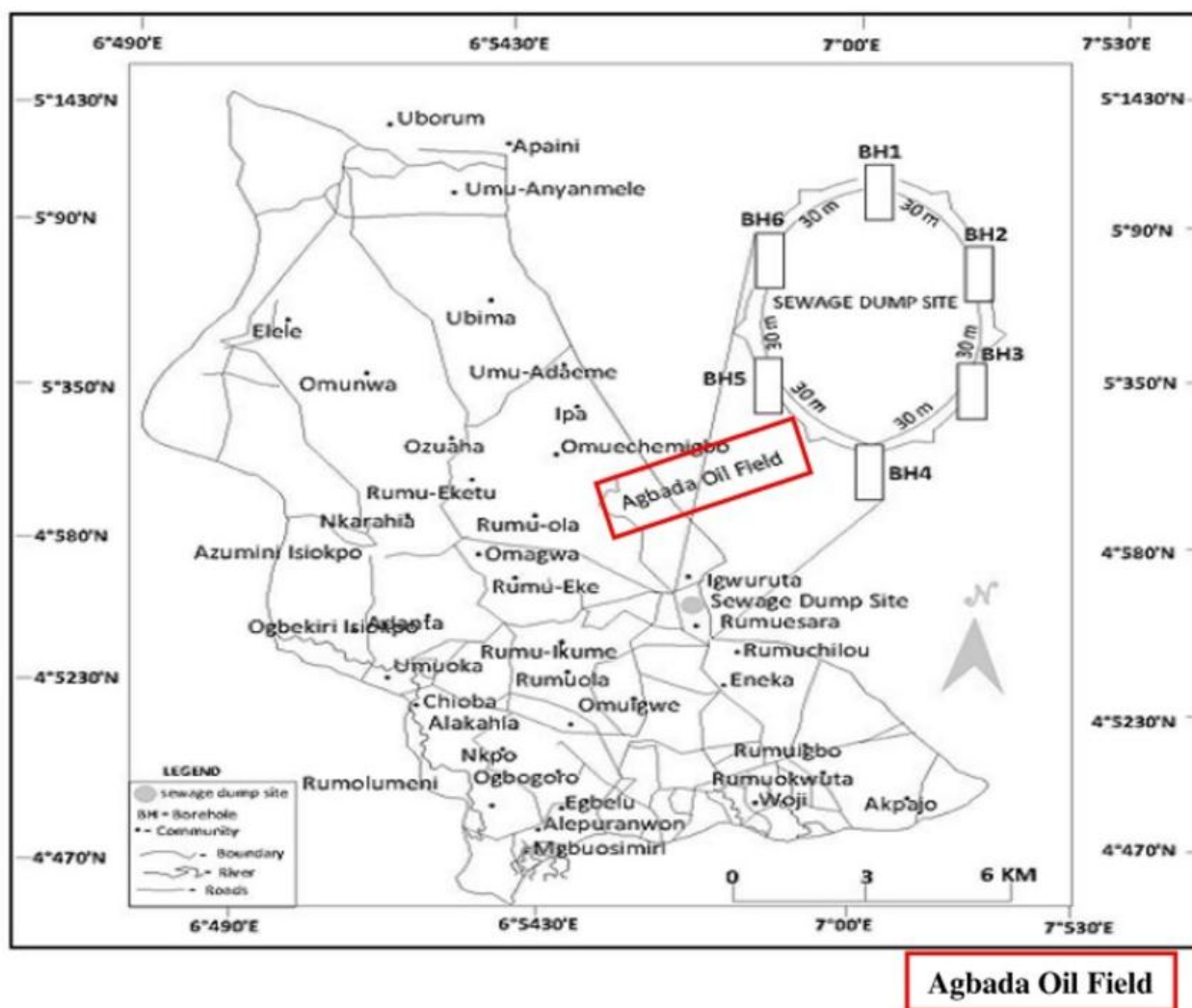


Figure 1. Site area of the collected soil sample.

2.4. Heavy Metal Determination

Iron (Fe) using spectrophotometer

Iron from the soil sample was identified using spectrophotometric assay method as described by Morris [27].

Soil digestion for heavy metal analysis

Five grams (5g) of the soil samples were digested in 250 ml conical flask by adding 30 ml of aqua regia (HNO_3 , HCl and HF in the ratio 3:2:1) and heated on a hot plate until volume remains about 7-12 ml as described by [13, 28]. The digest were filtered using what-man filter paper and the volume was made up to the mark in a 50ml volumetric flask, and will then be stored in a plastic container for atomic absorption spectra (AAS) analysis.

Fourier transform infrared (FTIR) spectra analysis

Fourier transform infrared (FTIR) spectra analysis of the impacted soil sampled from Agbada oil field were recorded at room temperature using 400 Perkin Elmer Agilent spectrometer (Perkin-Elmer, Norwalk, CA, USA) as described by Antonio *et al.* [7]. Spectra produced from the Agilent ma-

chine was recorded from 4000 cm^{-1} to 500 cm^{-1} wavelength numbers. Samples were thoroughly pasted with KBr at a sample/KBr ratio of 1:40. Spectra were obtained with a resolution of 4 cm^{-1} and were averaged over 32 scans.

2.5. Statistical Analysis

Data generated from the study were subjected to single way analysis of variance and the analysed empirical was presented as mean \pm SD.

3. Results

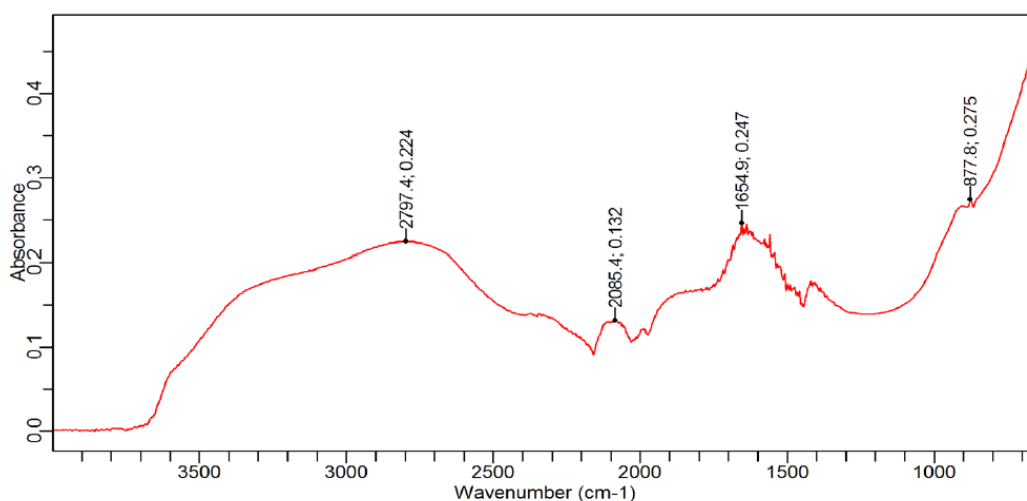
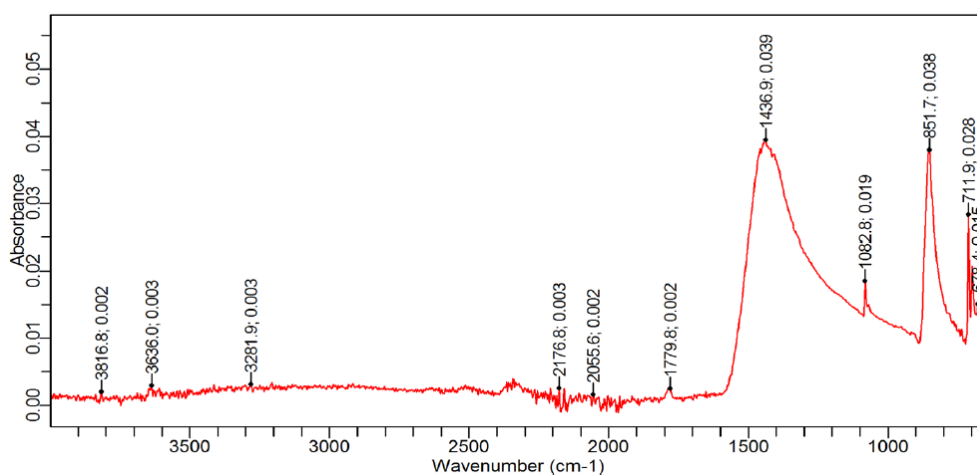
Tables below show the heavy metals bio-presence in the sampled petroleum hydrocarbon impacted soil from Agbada oil field, Rivers state, Nigeria. From the table respectively clinical implicated heavy metals such as As, Cd, Ni and Mn were found below detectable limits in all the samples.

Table 1. Heavy metal quantification in the soil samples.

Heavy metals	Control	point 1
Iron (Mg/ml)	3.52±0.2a	14.01±0.05b
Cadmium(Mg/ml)	BDL	BDL
Nickel (Mg/ml)	BDL	BDL
Arsenic(Mg/ml)	BDL	BDL

Heavy metals	Control	point 1
Lead (Mg/ml)	BDL	4.56±0.15c
Manganese (Mg/ml)	BDL	BDL
Copper (Mg/ml)	1.08±0.45c	3.22±0.25c

BDL= BELOW DETECTABLE LIMIT n=3

**Figure 2.** FTIR spectroscopy analysis of reference soil sample.**Figure 3.** FTIR spectroscopy analysis of impacted soil sample.

4. Discussion

In this oil-rich region, there is currently an unparalleled surge in the upstream and downstream operations of the oil and related industries [15, 3]. According to Valero [42], these oil firms and their allies have produced a wide range of pol-

lutants over time, including gaseous emissions, oil spills, effluents, and solid wastes, which have severely contaminated the environment. It is noted that these frontier companies only take fewer oil barrels into the drilling process because many of the petroleum compounds are lined within the oil muds, despite the pollution and various vulnerabilities created during the drilling of these petroleum compounds within

the oil muds of the oil refineries.

The current investigation involved the measurement of heavy metals and related chemicals in soil samples affected by petroleum hydrocarbons. Using an atomic absorption spectroscopy equipment, heavy metal analysis revealed that, for the test and control experiments, respectively, Fe was $14.01 \pm 0.05b$ and $3.52 \pm 0.2a$ mg/ml. Cu was measured in the test and control experiments at $3.22 \pm 0.25c$ and $1.08 \pm 0.45c$ mg/ml, respectively, while Pb was only detected in the test experiment at $4.56 \pm 0.15c$ mg/g. In both treatments, Cd, Ni, As, and Pb were found to be below detectable limits, however Mn was determined to be 0.011 in only the test trial. The outcome is consistent with research conducted by Onugbolu and Adieze [11, 13, 15, 27] on the physicochemical characteristics of spent engine oil spilled sites within artisanal workshops in Enugu state. Their findings revealed that heavy metals Fe and Zn were absent from the site, while tests on Hg, Pb, and As revealed levels below detectable limits. WHO [44] states that Pb can displace calcium from fish, animals, and bone. It also sustains toxicity from free heavy metals, chemicals, and radicals by covalently attaching to sulfhydryl bonds, which deactivates enzymes connected to cysteines [3]. Moreover, multiple clinical studies have demonstrated that elevated cadmium levels in the body can harm various organs such as the liver, kidney, and testes [4-9, 21-24].

Lately numerous investigations [32-37, 40-43] has demonstrated that nearly all human cancers like lung and prostate cancer can be ascribed to dietary sources.

The impacted soil was found to have characteristic absorption bands at 3244.6 cm^{-1} – 3842.9 cm^{-1} (O–H stretching), 2165 – 2366.9 cm^{-1} (CH–stretching), 1654 cm^{-1} and 1718.3 cm^{-1} (Amide I), 1436.9 cm^{-1} (Amide III), and 1407.1 cm^{-1} (–NH₂ bending) according to a Fourier transform infrared spectroscopy analysis of the table water for bisphenol A related compounds. Its saccharide structure is typified by the absorption bands at 902.1 – 687.7 cm^{-1} (skeletal vibrations involving the C–O stretching) and 1069.7 cm^{-1} 45 (anti-symmetric stretching of the C–O–C bridge). For some rubber package water, Antonino et al. (2017) found that the absorption bands were as follows: 3450 cm^{-1} (O–H stretching), 1870 – 2880 cm^{-1} (CH–stretching), 1655 cm^{-1} (Amide I), 1580 cm^{-1} (–NH₂ bending), and 1320 cm^{-1} (Amide III). Its saccharide structure is typified by the absorption bands at 1160 cm^{-1} (anti-symmetric stretching of the C–O–C bridge) and 1082 and 1032 cm^{-1} (skeletal vibrations involving the C–O stretching). The elimination of skeletal vibrations by carbonyl bond stretching in Malaysian bottle water was reported by Ezenwelu et al. [19] in 46 cases.

5. Conclusion

The study has demonstrated the health risks associated with petroleum hydrocarbon pollution in our city and other nearby locations. Endocrine disruptors, such as bisphenol-A, and heavy metals that are known to be health risks can be

detrimental to human and related biosystems. Many exploration businesses' standard operating procedures (SOP) require a comprehensive quality review and revision by government regulatory agencies. As a result, regulatory bodies face the difficulty of being truthful and up to date with their actions in order to uphold reason and strict guidelines for enterprises engaged in oil drilling, exploration, and production.

Abbreviations

FTIR	Fourier Transform Infra-red Spectroscopy
C-O	Carbonyl
Cu	Copper
Fe	Iron
Zn	Zinc
BDL	Below Detectable Limit

Author's Contributions

Ezenwelu, Chijioke, Obinna: Conceived and designed the experiments, performed the experiment and processed the data, analyzed the data and wrote the manuscript.

Ilechukwu, Cyril. Chijioke: Co-supervised the research and revised the manuscript.

Onwah, Joy: Carried out the experiment and processed the manuscript.

Chigbo, Malachy Chidiebere: Analyzed the research design and methodology, interpreted the data.

Iloanaya, Lauretta, Eberechukwu: Guided the experimental design and performed the experiment

Oparaji, Emeka Henry: Guided the experimental design, supervised the research, performed the experiment interpreted the data, revised the manuscript and processed the data.

Ethics

Authors declared no ethical issues that may arise after the publication of this manuscript.

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Conflicts of Interest

The authors declare no conflicts of interest.

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