

Heavy Metals Contamination and their Potential Toxicity in Petroleum Sludge Impacted Soils from Itsekiri Communities, Delta State, Nigeria

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Authors' contributions

This work was carried out in collaboration between both authors. Author DMS designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. Authors UMU and DMS managed the analyses of the study. Author UMU managed the literature searches. Both authors read and approved the final manuscript.

Article Information

DOI: 10.9734/CSJI/2018/42973

Editor(s):

(1) R. Rajalakshmi, Department of Chemistry, University Coimbatore, India.

Reviewers:

(1) Sana Sungur, Mustafa Kemal University, Turkey.

(2) Liliane Catone Soares, Federal University of Ouro Preto, Brazil.

(3) V. Vasanthabharathi, Annamalai University, India.

Complete Peer review History: <http://www.sciencedomain.org/review-history/26058>

Original Research Article

Received 02 June 2018

Accepted 06 August 2018

Published 31 August 2018

ABSTRACT

The concentrations of some heavy metals (Chromium, Cadmium, Lead, Nickel, Copper, Cobalt, Manganese, Iron and Zinc) in petroleum sludge impacted soils were determined to evaluate their contamination levels using atomic absorption spectrophotometer. The petroleum sludge samples were collected from the discharge pit of Warri Refinery and Petrochemical Company (WRPC) while the soil samples were collected from five selected oil-impacted communities (Ubeji – 500 m, Ekpan – 1.5 km, Aja-Etan – 2.5 km, Ifie-Kporo – 3.0 km, Ijala-Ikenren – 3.8 km from Warri refinery and were coded A, B, C, D and E respectively). A control sample was also collected 8.5 km away from the refinery. The results obtained revealed that with the exception of Fe, the sludge samples contained the highest concentrations (in mg/kg dry weight) of Chromium (2462.6±0.5), Lead (406.7±0.2), Copper (201.3±0.0), Manganese (8335.1±0.9) and Zinc (1009.2±0.3) while Iron was highest (10313.5±2.3) in site A. All the metals were higher in the studied sites than the control sites and a stepwise decrease in metal contents were observed from A to E. Some geochemical

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assessment techniques, including enrichment factor (EF) and geoaccumulation index (Igeo), were used to determine the levels of metal toxicity in the sediments. Computed enrichment factors showed that the soil samples have suffered significant systematic heavy metals enrichment following proximity to the refinery. Values of geoaccumulation index (Igeo) indicated different contamination and toxicity levels of Chromium, Cadmium, Lead, Copper, Manganese, and Zinc while Nickel was not detected.

Keywords: Oily sludge; heavy metals; impacted soils; enrichment factor; geo-accumulation index.

1. INTRODUCTION

In view of the petroleum refining operations in the Niger Delta region of Nigeria, a large volume of oily sludge is being produced every year. Reports have shown that 1 ton of petroleum sludge is produced out of 500 tons of crude oil [1]. Oily sludge is a recalcitrant residue characterized as a stable water-in-oil (W/O) emulsions of water, solids, petroleum hydrocarbons, and heavy metals [2,3,4], thus being categorized as hazardous waste [5]. Industrial and hazardous waste management is one of the most significant problems because of the high risk of leaching into the environment. Poor waste disposal of the oily sludge impacts negatively on soil biological, chemical and physical characteristics such as the structure, biodiversity, microbial populations, nutrient cycles, reduction of moisture content, relatively low organic matter content, etc. The situation is increasingly becoming a concern to the people of the area as oil companies are expanding and waste treatment facilities are either inadequate or not available.

In recent times, environmental contamination by heavy metals has become a worldwide problem due to the fact that heavy metals, unlike some other contaminants, are non-biodegradable [6]. Consequently, they are not detoxified but are bio-accumulated in the soil environment. Heavy metal refers to any metallic element whose density is relatively equal to or greater than 5 g/cm^3 and is toxic even at low concentration [7]. Contamination of soils with heavy metals poses a long term risk to the groundwater and ecosystem. Most importantly, soil contamination by heavy metals has serious health implication especially with regards to plants grown on such soils and the animals that depend on them [8,9]. Long-term effect of heavy metal exposure to human and higher animals includes mental lapse, kidney failure, and central nervous system disorder [9,10,11]. For example, chronic exposure to Cd can have harmful effects such as lung cancer, bone fractures, kidney dysfunction,

hypertension. Exposure to lead (Pb) may cause plumbism, anemia, nephropathy, gastrointestinal colic, and central nervous system symptoms [10,11,12].

Organic and inorganic substances, which include varied heavy metals, synthetic or natural occurring organic compounds [particularly petroleum hydrocarbons (PHCs)], all constitute the main mix of environmental contaminants in nature. These chemical contaminants are found naturally, however, due to anthropogenic activities they become more intense and get released into the environment. A contaminated site thought to encompass a blend of metals and organics are generally considered to be difficult to remediate due to the mixed nature of the contaminants [4,13,14]. Such a gamut of heavy metals and PHCs emanating from refining activities coupled with scrupulous agricultural practices distort organic matter decomposition via the natural bacterial flora [14,15,16]. 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 [4,17]. Defects in petroleum sludge management in form of releasing the waste into the environment is the current most attended concern [18]. Heavy metals occupy a special position in soil chemistry because they play very important physiological roles in nature [19,20]. Generally, topsoil layer contains largest amount of contaminants and its concentration in soil mainly depends on the adsorption properties of soil matter. The chemical composition of oily sludge varies over a wide range, depending on crude oil source, processing scheme, equipment and reagents used in the refining process.

Considering the complexity and unknown compositions of different sludge from different spots, there is not any distinctive formula to estimate its impact on any environmental media. Thus, chemical and physical analyses must be conducted to assess the exact compositions and

elements present in the oily waste and the impacted soil samples [21]. On the basis of these characteristics, an investigation of the contamination levels of some heavy metals in oily sludge impacted soils from Itsekiri (an area in close proximity to Warri refinery in Delta State of Nigeria) has been carried out, in order to get a better understanding of the quality of sediments and assess the ecological risk through a thorough examination of the impact of industrial waste (oily sludge) on these sediments.

2. MATERIALS AND METHODS

2.1 Description of Sampling Sites

The Niger Delta is one of the world's largest deltas and makes up approximately 7% of the land area of Nigeria. It has been reported to cover an area of approximately 75,000 km², representing about 7.5% of Nigeria [16]. The region has about 5284 oil wells and 527 flow stations of crude oil processing with more than 7000 km of oil and gas pipeline traversing across the whole land area (Fig. 1). Delta State which is being nicknamed "The Big Heart of the Nation" lies approximately between Longitude 5°00 and 6°.45' East and Latitude 5°00 and 6°30' North of

the equator. It is located in southern Nigeria with an area of 17,698 km² (6,833 sq mi) and a population of 4,112,445 as of 2006 [22,23]. It is made up of 25 Local Government Areas and comprising mainly five major ethnic groups: Urhobo, Isoko, Anioma and Ukwani, Ijaw and Itsekiri (Fig. 2). Warri is the biggest commercial city in the state where the refinery is located. The major people in Warri comprise the Urhobos, Ijaws and Itsekiris [23,24].

The oil spill impacted communities (Itsekiri) are situated between Latitudes 5°30'N and 5°33'N of the Equator and Longitudes 5°45'E of the Prime Meridian, in Warri South Local Government Area of Delta State. Climatologically, the study area has a mean annual rainfall of 3200 mm and a mean temperature of about 28°C. Topography is flat, with an average elevation of about 13 m above sea level. The flat and low relief features often encourage flooding after rain events. The drainage pattern is dendritic with major tributaries emptying into the Forcados River. The vegetation of the area is tropical rain forest type, comprising abundant trees and grasses. The soils in the study area exhibit a wide range of colours from milky white through brown to very dark brown, and they vary in types and



Fig. 1. Map showing wide distribution of Shell Petroleum Development Corporation (SPDC) oil fields in the Niger Delta region, adapted from Nwilo and Badejo [25]

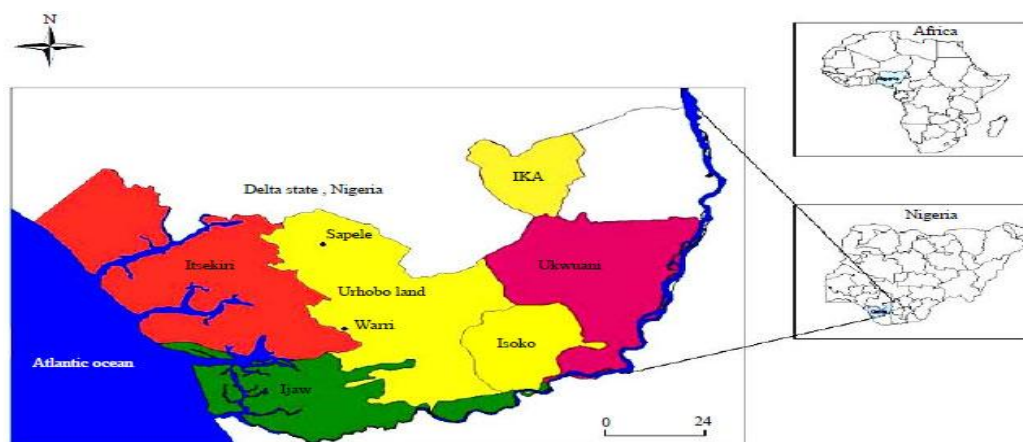


Fig. 2. Map of Delta state showing the study area

texture from loamy to sandy and clayey types according to the United States Department of Agriculture (USDA) classification. Warri people are mainly farmers, civil servants, businessmen and women, artisans and entrepreneurs. Due to frequent oil spills from the sludge pits as a result of refining operations from the Warri Refinery and Petrochemical Company (WRPC), the Itsekiri people are faced with the problem of environmental degradation.

2.2 Sample Collection, Handling and Preservation

US EPA (SW-846) guidelines were applied, using composite sampling for collecting sediment samples where sub-samples were collected from randomly selected locations in an area. Five (5) oily sludge samples were collected from the discharge pit of WRPC with core sampler in a 500 mL wide-mouth glass jar and pooled. Also, fifty (50) soil samples were randomly collected using soil auger from the depth of 0-15 cm from five selected oil-impacted communities (Ubeji – 500 m, Ekpan – 1.5 km, Aja-Etan – 2.5 km, Ifie-Kporo – 3.0 km, Ijala-Ikenren – 3.8 km from WRPC and were coded A, B, C, D and E respectively) and stored in sealed polythene bags (Table 1). There were ten (10) replicates for each sampling site and the sub-samples were thoroughly mixed to obtain a representative sample of each. A control sample was also collected 8.5 km away from WRPC. These were stored in well-labeled amber glass bottles with a teflon-lined screw cap, held at 4°C immediately in a cooler of ice and transported to the laboratory for pre-treatment and analyses [26,27]. The soil samples were air-dried for two weeks, rolled manually, mixed and sieved with 2

mm mesh to remove stones and debris. These were properly stored in well-labeled air-tight containers until analysis.

A table depicting the identity, classification, geographical location, chemical and physical (textural analysis) characteristics of soils is given (Table 1).

2.2.1 Reagents

All chemicals and reagents were of analytical grade and of highest purity possible. They were supplied by BDH Labs (UK). BDH Chemicals Limited Poole England.

2.3 Physicochemical Analysis

Physicochemical properties such as pH, conductivity, soil texture, organic matter, cation exchange capacity (CEC) were analyzed. The pH and electrical conductivity were measured in a soil suspension (1:10 w/v dilution) by digital pH meter (Jenway model 3015) and conductivity meter (Systronics-304), respectively. Organic matter was examined by the Potassium dichromate titration method [28]. Cation exchange capacity (CEC) of soil was determined as per the procedure outlined by Useh et al. [9]. The texture of the soil was determined by using the hydrometer method [29].

2.4 Heavy Metals Analysis

A test portion of 1.00 g of each soil sample was digested using the conventional aqua regia (3:1, v/v, HCl to HNO₃) digestion procedure. The soil sample was weighed and transferred into the digestion vessel (250 ml glass beaker covered

with watch glass). 20 ml of freshly prepared aqua regia mixture was added and mixed by swirling. This was moistened with a little deionized distilled water. Thereafter, the digestion vessel was placed on a heating mantle for 2 h at 110°C until about 5 ml of digest remained in the flask. The vessel was removed and allowed to cool for 15 min. Then, another 20 ml of freshly prepared aqua regia mixture was added and boiling was repeated until the digest cleared up. After evaporation to near dryness, the sample was allowed to cool and was diluted with 20 ml of 2 % (v/v with H₂O) HNO₃ and transferred into a 100 ml volumetric flask after filtering through Whatman no. 42 paper and was made to volume with deionized distilled water. The blank solutions were undergoing the same digestion procedure as that of the sample. For the oily sludge sample, most recently US EPA Method 3031 for acid digestion of oily sludge for metals was applied with little adjustment [18].

All digestions were carried out in triplicates for each sample and the amounts of trace metals recorded as the mean value. The extracts were analyzed for heavy metals (Cr, Cd, Pb, Ni, Cu, Co, Mn, Fe and Zn) using atomic absorption spectrophotometer (AAS) iCE 3000 Series 3000 at their respective wavelength (357.9, 228.8, 283.3, 232.0, 324.8, 240.7, 279.5, 248.3 and 213.9 nm) according to APHA method [30].

2.4.1 Preparation of calibration standards

For calibration of the instruments, a series of five standard solutions were prepared by serial dilution of the stock standard solutions (1000 mg/l) of the metals to be analyzed.

2.4.2 Preparation of spiking standards

For the spiking processes of the soil samples, a mixture of standard solution containing 1 mg/L of each Cr, Cd, Pb, Ni, Cu, Co, Mn, Fe and Zn was prepared by serial dilution from 1000 mg/L stock standard solution in to 100 ml volumetric flask and diluting to the mark with deionized distilled water.

2.4.3 Determination of heavy metals in sample matrices

The digested samples were analyzed for the heavy metal concentrations such as Cr, Cd, Pb, Ni, Cu, Co, Mn, Fe and Zn using Atomic

Absorption Spectrometer (FAAS) (AAS iCE 3000 Series).

2.5 Quality Assurance and Quality Control

All analyses were carried out in triplicates and the values reported are the mean values of the replicate analyses. Quality Assurance was also guaranteed through the use of blanks to check for background contamination and other sources of error by the reagents and equipment used. The accuracy of the method was determined by matrix spike recovery studies and precision was expressed as the relative standard deviation (RSD) of replicate results. Metal recovery test was carried out by spiking in triplicates each soil sample with a metal standard solution of 1.0 mg/l of the analytes of interest, digested and analyzed using the same analytical procedure as the soil samples. The percentage recoveries of the analyte were calculated by using the following equation:

$$\% \text{ Recovery} = \frac{\text{conc. in the spiked sample} - \text{conc. in unspiked sample}}{\text{actual spike conc}} \times 100$$

where, conc. = concentration of metal of interest

The relative standard deviation for replicate analyses of the same sample was obtained by dividing the standard deviation by the mean value of the analytical data according to the following equation:

$$\% \text{RSD} = \frac{\text{standard deviation}}{\text{mean value}} \times 100$$

2.6 Statistical Analysis

In order to quantitatively analyze and confirm the relationship among soil physicochemical properties and heavy metals content, Pearson correlation analysis was applied to the dataset.

All the statistical analyses were performed using statistical software SPSS Windows version 16.0 with a level of significance of $p < 0.05$ [21].

2.7 Toxicity Assessment of Sediment Samples

Some geochemical assessment techniques, including enrichment factor (EF) and geoaccumulation index (I_{geo}), were used in order to determine the levels of metal contamination in the sediments in focus [31]. The

Table 1. Selected physicochemical parameters of the Sludge and soil samples

Parameters	Sludge	Site a	Site b	Site c	Site d	Site e	Control
pH	5.3±0.1	5.3± 0.3	5.4±0.6	5.4±0.0	5.5±0.5	5.5±0.0	7.8±2.0
Conductivity (µs/cm)	0.6±0.0	0.6± 0.0	0.6±0.0	0.5±0.1	0.5±0.0	0.4±0.0	0.3±0.0
Soil texture	Black viscous liquid	Clay	Silty clay	Silty loam	Sandy clay loam	Sandy loam	Loamy sand
Sand (%)	-	8.2± 0.1	12.6±1.0	47.4±0.0	58.2±0.0	74.4±0.1	58.1±0.0
Silt (%)	-	30.5 ± 0.2	40.6±0.0	27.5±0.0	14.8±0.0	5.1±0.0	31.6±0.4
Clay (%)	-	61.3± 0.0	48.8±0.0	25.1±0.2	27.0±0.1	20.5±0.0	10.3±0.0
CEC (mg/kg)	358.0± 0.0	291.0 ± 0.0	249.4 ±0.0	108.2 ±0.0	209.6 ±0.0	176.2 ±0.0	96.4±0.0
Organic matter (%)	56.8±2.1	31.5±0.0	28.6±0.1	26.7±1.4	23.0±0.0	17.3±0.2	7.4±0.0

ND = Not detected. The results are means of triplicate determination ± standard deviation

computation of enrichment factor (EF) has been adopted to evaluate the impact of anthropogenic activities related to the metal abundance in sediments. According to Moez et al. [32], EF is defined by the following equation:

$$EF = \frac{(C_X/C_{Fe})_{\text{sample}}}{(C_X/C_{Fe})_{\text{crust}}}$$

Where by

- Fe (iron) is chosen as a natural element of the reference
- $(C_X/C_{Fe})_{\text{sample}}$ is the ratio between the concentration of the element "X" and that of Fe in the sediment sample
- $(C_X/C_{Fe})_{\text{crust}}$ is the ratio between the concentration of the element "X" and that of Fe in unpolluted reference baseline.

According to Birch [33], calculated EF values could be interpreted as follows:

- $EF \leq 1$: no enrichment;
- $1 < EF < 3$: minor enrichment;
- $3 < EF < 5$: moderate enrichment;
- $5 < EF < 10$: moderate-to-severe enrichment;
- $10 < EF < 25$: severe enrichment;
- $25 < EF < 50$: very severe enrichment;
- $EF > 50$: extremely severe enrichment.

The study of geoaccumulation index (I_{geo}) could be relevant in the examination of the contamination level of the sediment samples affected by metals. In Maurizio's [34] view, I_{geo} can be obtained by the following equation:

$$I_{geo} = \text{Log}_2 \left(\frac{C_n}{1.5B_n} \right)$$

whereby C_n is the concentration of the metal (n) in sampled and analyzed sediment and B_n is the background concentration of the same metal (n) and factor 1.5 is the background matrix correction factor due to lithogenic effects [35]

According to Maurizio's [34], calculated I_{geo} values could be interpreted as follows:

- $I_{geo} \leq 0$: Uncontaminated
- $0 < I_{geo} < 1$: From uncontaminated to moderately contaminated
- $1 < I_{geo} < 2$: Moderately contaminated

- $2 < I_{geo} < 3$: From moderately contaminated to strongly contaminated
- $3 < I_{geo} < 4$: Strongly contaminated
- $4 < I_{geo} < 5$: From strongly to extremely contaminated
- $I_{geo} > 5$: Extremely contaminated

3. RESULTS AND DISCUSSION

Heavy metals are useful for biological growth and development but when they are introduced at higher concentrations via leaching or chemical reactions from storage tanks, petroleum pipelines, other mechanical components of the refinery facilities etc. into the environment, they become toxic. Data obtained in this current study (Table 2) revealed that with the exception of iron, the sludge samples contained the highest concentrations of chromium (2462.6 ± 0.5 mg/kg), lead (406.7 ± 0.2 mg/kg), copper (201.3 ± 0.0 mg/kg), manganese (8335.1 ± 0.9 mg/kg) and Zn (1009.2 ± 0.3 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 soils around the WRPC, iron was highest (ranging from 10313.5 ± 2.3 mg/kg in site A to 7429.8 ± 1.4 mg/kg in site E) of all studied metals. It has been confirmed that natural soils contain a significant concentration of iron [36]. The suggestion has been made that the contamination of the environment by iron cannot be conclusively linked to waste materials alone but to other natural sources as well [37]. Manganese was the second most abundant element as determined in the soil samples and it ranged from 8004.2 ± 0.3 mg/kg in site A to 5628.1 ± 0.2 mg/kg in site E which was higher than the control site (2011.1 ± 0.3 mg/kg). Manganese levels in this study are higher than those reported earlier in our previous work [18]. Manganese in trace amounts is an essential element for both plants and animals and it is among the trace elements. Exposure to an abnormally high concentration of manganese particularly in the form of dust and fumes is known to have resulted in an adverse effect on humans. Interference with iron metabolism especially haemoglobin formation was one of the first toxic effects of manganese [18]. Manganese in the form of oxide is a component of subsoil materials so its level of concentration could be as a result of this. The higher concentration of various heavy metals in soil samples is attributed to their release from industrial effluents. The

numerous processes and facilities within the refinery, coupled with the procedure of handling as well as storage of its byproduct serve as avenues for the release of these metals into the environment.

Table 2 revealed a stepwise decrease in metal contents across the sampling sites studied, as each site is further apart from the WRPC except for sites D and E in the case of Cr and Co. The values of Cadmium recorded in the study areas ranged from 3.6 ± 0.1 mg/kg in site A to 1.1 ± 2.8 mg/kg in site E. Cadmium concentrations at the control site was 0.6 ± 1.1 mg/kg and was well below the values obtained from samples at the contaminated site. The Cd values in the study area were relatively lower than 9.11 mg/kg recorded from soils within the vicinity of NNPC depot Jos, Nigeria by Moreira et al. (2014) but significantly higher than 0.60 mg/kg obtained at automobile mechanic site in Benue, north-central Nigeria by Karami and Shamsuddin [38].

Lead concentration ranged from 157.6 ± 0.2 mg/kg in site A to 113.0 ± 0.1 mg/kg in site E. These values were higher than that obtained for control sample and also higher than 15.1 mg/kg reported by Bierkens and Geerts [39] as well as 14.13 mg/kg reported by Raji and Abejide [40].

Inhalation and ingestion are the two main routes of Pb exposure to humans and other vertebrates. Lead finds its way and accumulates in the brain and could lead to death, gastrointestinal tract, kidney as well as central nervous system disorder. Other health risks associated with lead include impaired growth, loss of memory, nausea, insomnia and anorexia. Ni was not detected in almost all the sites except in site A and the sludge samples. Concentrations of Cu and Zn ranged from 26.1 ± 0.0 to 11.3 ± 0.1 mg/kg and 916.3 ± 0.2 to 515.4 ± 0.2 mg/kg in sites A to E respectively which were lower than their controls indicating some levels of accumulation of these trace metals in soils within the vicinity of WRPC. The levels of Cu determined in the study area were higher than value (2.78 mg/kg) of Nathanail et al. [41] but lower than 52.14 mg/kg and 77.0 mg/kg reported by Chorom et al. [42] and Towell et al. [41] respectively. The value of Zn in this present study was well above 0.03 to 5.5 mg/kg and 25.06 mg/kg reported by Valls and de Lorenzo [44] and Orji et al. [45] respectively. Copper and zinc are essential macronutrients required for both plants and

animal health. High doses of Cu are associated with anaemia, liver and kidney damage as well as irritation of both stomach and intestine [44]. Excess doses of Zn in the soil retard the breakdown of organic matter by influencing the activity of microorganism and earthworm [46].

3.1 Accuracy and Precision

The results of accuracy and precision were evaluated through recovery tests. Matrix spike recovery studies determined the accuracy of the method and precision was expressed as the relative standard deviation (RSD) of replicate results and the results are recorded (table 3). As can be seen, the percentage recovery of the metal analysis in the soil ranged between 91.1–100.1% and the RSD values ranged from 1.2–19.8%. The matrix spike recovery obtained in this study falls within the normally acceptable range of 90–110% for a good recovery study. The high percentage recovery obtained from the study validates the accuracy of the method and the reliability of the levels of metal concentration in this study. The RSD values of the samples were < 20%, indicating that the proposed method was precise.

3.2 Ecological Risk Assessment

Enrichment factors (EF), were calculated with respect to Fe which was the most abundant metal as mentioned in "Toxicity Assessment of Sediment Samples" section. Computed enrichment factors (EF) have revealed that most of the values exceeded 1, especially for Cr, Pb, Zn, Cu, Mn and Cd, indicating an important anthropogenic effect approved by a significant metallic contamination of the majority of the studied samples. The extremely severe enrichment of Cr, Pb and Cu in the oily sludge is in order since it is the contaminant factor. Also, there was no enrichment of Ni in all the studied sites (Figs. 3A, 3B). Geoaccumulation index (I_{geo}) computation for the sediment samples is recorded, summarized and interpreted (Table 4, Fig. 4). As for Cd, Cu, Mn and Zn sediment quality was moderately contaminated in all the studied sites while for Cr, sediment quality varied from moderately contaminated to strongly contaminated especially in site A. More so, the sludge which is the contaminant was extremely enriched with Cr, Cd, Pb and Cu while Ni was not detected in all the studied sites.

Table 2. Heavy metals concentrations of the samples (mg/kg)

Heavy metals	Sludge	Site a	Site b	Site c	Site d	Site e	Control
Cr	2462.6±0.5	166.8±0.3	116.7±0.2	97.9±0.1	83.6±0.1	90.9±0.1	23.9±0.1
Cd	4.0±0.0	3.6±0.1	2.3±0.0	1.8±1.1	1.6±0.4	1.1±2.8	0.6±1.1
Pb	406.7±0.2	157.6±0.2	144.9±0.2	126.2±0.1	119.5±0.2	113.0±0.1	28.5±0.1
Ni	59.6±0.2	29.6±0.0	ND	ND	ND	ND	ND
Cu	201.3±0.0	26.1±0.0	20.2±0.0	20.0±0.0	14.3±0.1	11.3±0.1	6.7±0.0
Co	29.9±0.0	22.9±0.0	11.6±0.0	11.5±0.0	13.6±0.0	12.0±0.0	10.9±0.0
Mn	8335.1±0.9	8004.2±0.3	7945.5±0.7	6111.8±1.3	5761.0±1.0	5628.1±0.2	2011.1±0.3
Fe	9305.5±2.4	10313.5±2.3	10061.9±2.0	9484.9±0.7	8567.8±1.4	7429.8±1.4	6057.1±2.1
Zn	1009.2±0.3	916.3±0.2	673.9±0.2	604.9±0.1	577.2±0.2	515.4±0.2	245.9±0.0

ND = Not detected, the results are means of triplicate determination ± standard deviation

Table 3. Recovery and precision test results of metals for soil matrix spike sample

Heavy metals	Conc. in unspiked sample(mg/kg)	Amount added (mg/kg)	Conc. in spiked sample (mg/kg)	Recovery (%)	RSD (%)
Cr	166.8±0.3	100	262.1 ±0.1	95.4 ±2.3	2.5
Cd	3.6±0.1	100	97.2 ±0.1	93.7 ±1.9	6.0
Pb	157.6±0.2	100	251.3 ±0.1	93.6 ±3.6	10.0
Ni	29.6±0.0	100	124.0 ±0.0	94.3 ±2.6	15.2
Cu	26.1±0.0	100	126.2 ±0.1	100.1±1.3	10.7
Co	22.9±0.0	100	115.6 ±0.1	92.7 ±1.7	19.8
Mn	8004.2±0.3	100	8100.7 ±0.1	96.5 ±1.5	1.2
Fe	10313.5±2.3	100	10404.6 ±0.1	91.1 ±2.6	6.1
Zn	916.3±0.2	100	1008.6 ±0.1	92.3 ±3.5	1.6

Table 4. Geoaccumulation index (*I*_{geo}) classification and ranges of heavy metals in the samples (mg/kg)

<i>I</i>_{geo}	Classes	Level of contamination	Cr	Cd	Pb	Ni	Cu	Co	Mn	Fe	Zn
<i>I</i> _{geo} ≤ 0	0	Uncontaminated	-	-	-	-	-	Sites B, C, D, E	-	Sites D, E	-
0 < <i>I</i> _{geo} < 1	1	From Uncontaminated to moderately contaminated	-	Sites D, E	-	-	Sites C, D, E	Sludge, Site A	Sites D, E	Sludge, Sites A, B, C	Sites B, C, D, E
1 < <i>I</i> _{geo} < 2	2	Moderately contaminated	Sites B, C, D, E	Sites A, B, C	Sites A, B, C, D, E	-	Sites A, B	-	Sludge, Sites A, B, C	-	Sludge, Site A
2 < <i>I</i> _{geo} < 3	3	From moderately contaminated to strongly contaminated	Site A	Sludge	-	-	-	-	-	-	-
3 < <i>I</i> _{geo} < 4	4	Strongly contaminated	-	-	Sludge	-	-	-	-	-	-
4 < <i>I</i> _{geo} < 5	5	From strongly to extremely contaminated	-	-	-	-	Sludge	-	-	-	-
<i>I</i> _{geo} > 5	6	Extremely contaminated	Sludge	-	-	-	-	-	-	-	-

Table 5. Pearson correlation coefficient matrix for selected physicochemical properties and heavy metals of the samples

	<i>pH</i>	Conductivity	Sand	Silt	Clay	CEC	OM	Cr	Cd	Pb	Ni	Cu	Co	Mn	Fe	Zn
<i>pH</i>	1.000															
Conduc-tivity	-0.890**	1.000														
Sand	0.414	-0.746	1.000													
Silt	0.280	-0.238	-0.154	1.000												
Clay	-0.364	0.305	-0.303	0.643	1.000											
CEC	-0.606	0.857*	-0.803*	-0.337	0.160	1.000										
OM	-0.648	0.871*	-0.789*	-0.423	-0.116	0.847*	1.000									
Cr	-0.270	0.545	-0.582	-0.622	-0.536	0.701	0.871*	1.000								
Cd	-0.624	0.874*	-0.904**	-0.186	0.222	0.893**	0.910**	0.688	1.000							
Pb	-0.546	0.776*	-0.694	-0.573	-0.299	0.829*	0.973**	0.950**	0.833*	1.000						
Ni	-0.321	0.627	-0.739	-0.477	-0.216	0.821*	0.874*	0.897**	0.873*	0.902**	1.000					
Cu	-0.297	0.576	-0.615	-0.597	-0.503	0.716	0.892**	0.999**	0.718	0.960**	0.907**	1.000				
Co	-0.384	0.671	-0.735	-0.475	-0.123	0.855*	0.864*	0.845*	0.898**	0.877**	0.989**	0.857*	1.000			
Mn	-0.901**	0.982**	-0.757*	-0.135	0.415	0.825*	0.813*	0.457	0.856*	0.706	0.569	0.490	0.610	1.000		
Fe	-0.823*	0.881**	-0.740	0.197	0.613	0.614	0.654	0.203	0.770*	0.474	0.371	0.248	0.424	0.911**	1.000	
Zn	-0.765*	0.941**	-0.825*	-0.284	0.236	0.899**	0.918**	0.660	0.978**	0.842*	0.821*	0.689	0.858*	0.923**	0.810*	1.000

** Correlation is significant at the 0.01 level (2-tailed). * Correlation is significant at the 0.05 level (2-tailed). '-' sign denoted negatively correlated.

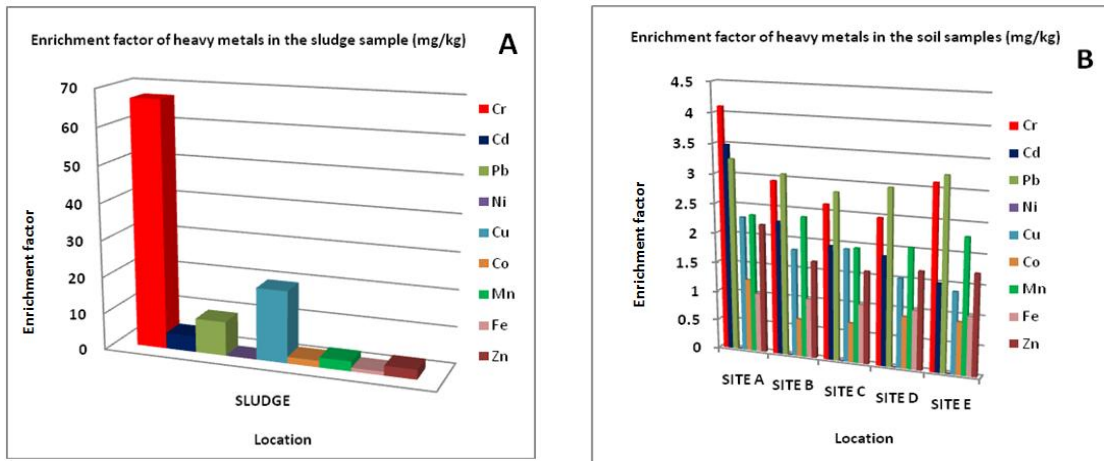


Fig. 3. Graphical representation of the enrichment factor across the study sites. A depicts enrichment in sludge, B depicts soil samples

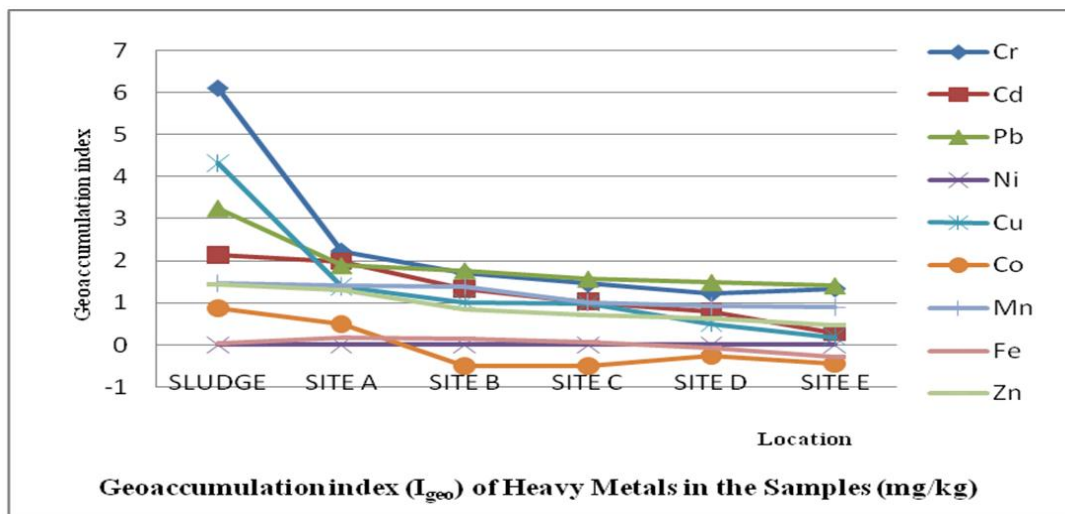


Fig. 4. Graphical representation of the Geoaccumulation index across the study sites

3.3 Assessment of Relationships of Soil Physicochemical Properties and Heavy Metals Content

Correlation analysis was made for 7 soil physicochemical properties and heavy metals content which indicated intra and inter-relationships among the soil properties. Of the 120 pairs in the correlation matrix, 53 pairs showed significant relationships among them (Table 5). A strong positive significant relationship was observed between conductivity vs Mn, Fe and Zn, CEC vs Cd and Zn, organic matter vs Cd, Pb, Cu and Zn, Cr vs Pb, Ni and Cu, Cd vs Co and Zn, Pb vs Ni, Cu and Co, Ni vs Cu and Co, and Mn vs Fe and Zn ($r = \text{or} > 0.9$,

$p < 0.01$). Also, strong negative significant correlations were seen between pH vs conductivity and Mn, sand and Cd, ($r = -0.9$, $p < 0.01$) (Table 5). However, most of the heavy metals were negatively correlated with pH which shows that increasing pH can reduce the metal availability. Further, moderately positive correlation was seen among most of the variables in the correlation matrix ($r = \text{or} > 0.8$, $p < 0.05$). A positive correlation among the metals in soil samples could indicate common sources of the metals which could be related to known geochemical associations among them while negative or insignificant positive correlation between the metals indicate that the appearance of local high concentration for one metal by

possible contamination does not necessarily indicate high values for other metals. It may also indicate different sources or biogeochemical behaviours [11]. Many other relationships between various quantitative variables are also significant with the least correlation values. These results of correlation can prove useful in understanding the relationships of metal concentrations with each other and with physicochemical properties of soils.

4. CONCLUSION

This study presented the findings from the heavy metals analysis of oily sludge impacted soil samples, collected from five sampling sites. Calculated enrichment factors and geo-accumulation index revealed that all the studied sites are considered contaminated with the selected heavy metals except Ni. Iron was the most abundant metal though not considered as the most contaminated in all the studied sites as this metal is widely distributed in nature. The presence of these heavy metals within the neighbouring environs to the refinery pose a threat to the soil because of its bioaccumulation, thereby creating a negative impact to the community. The elevated concentrations of the assayed environmental heavy metals further project the damaging effects of the petroleum waste disposal practices in the region. The results of the study could be utilized as a baseline towards the development and implementation of adequate remediation techniques to reclaim the affected sites.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Hentati O, Lachhab R, Ayadi M, Ksibi M. Toxicity assessment for petroleum-contaminated soil using terrestrial invertebrates and plant bioassays. *Environmental Monitoring and Assessment*. 2013;185:2989-2998.
2. Said WA, Lewis DL. Quantitative assessment of the effects of metals on microbial degradation of organic chemicals. *Applied Environmental Microbiology*. 2007;5(7):1498-1503.
3. Abioye OP, Agamuthu P, Abdul-Aziz RA. Biodegradation of used motor oil using organic waste amendment. Hindawi Publishing Corporation; 2012.
4. Moreira IT, Oliveira OM, Triguís JA, Queiroz AF, Barbosa RM. Evaluation of the effects of metals on biodegradation of total petroleum hydrocarbons. *Microchemistry Journal*. 2013;1(10):215–220.
5. Cerqueira VS, Peralba MR, Camargo FA, Bento FM. Comparison of bioremediation strategies for soil impacted with petrochemical oily sludge. *International Journal of Biodeterioration and Biodegradation*. 2014;9(5):338–345.
6. Ali H, Khan E, Sajad MA. Bioremediation of heavy metals—concepts and applications. *Chemosphere*. 2013;91(7):869–881.
7. Yao Z, Li J, Xie H, Yu C. Review on remediation technologies of soil contaminated by heavy metals. *Procedia Environmental Science*. 2012;1(6):722–729.
8. Merrill JC, Morton JJP, Soileau SD. Metals: Cadmium. In: Hayes AW (ed) *Principles and methods of toxicology*, 5th edn. Taylor and Francis, London. 2007; 665–667.
9. Useh MU, Etuk-Udo GA, Dauda MS. Evaluating the physico-chemical properties and heavy metals in soils of municipal waste dumpsites at Kubwa, Abuja, Nigeria. *Journal of Chemistry and Chemical Sciences*. 2015;5:654-662.
10. Khan SR, Kumar JIN, Kumar RN, Patel JG. Physicochemical properties, heavy metal content and fungal characterization of an old gasoline-contaminated soil site in Anand, Gujarat, India. *Environmental and Experimental Biology*. 2013;11:137–143.
11. Cheraghi M, Sobhanardakani S, Lorestani B, Merrikhpour H, Parvizi Mosaed H. Biochemical and physical characterization of petroleum hydrocarbon contaminated soils in Tehran. *Journal of Chemical Health Risks*. 2015;5:199–208.
12. Prashanth L, Kattapagari KK, Chitturi RT, Baddam VRR, Prasad LK. A review on role of essential trace elements in health and disease. *Journal of Dr. NTR University of Health Sciences*. 2015;4:75-85.
13. Roane TM, Josephson KL, Pepper IL. Dual bioaugmentation strategy to enhance remediation of cocontaminated soil. *Applied Environmental Microbiology*. 2001;6(7):3208-3215.
14. Olajire AA, Altenburger R, Küster E, Brack W. Chemical and ecotoxicological assessment of polycyclic aromatic

- hydrocarbon—contaminated sediments of the Niger Delta, Southern Nigeria. *Science of the Total Environment*. 2005;3(4):123-136.
15. Ekundayo EO, Obuekwe O. Effects of an oil spill on soil physicochemical properties of a spill site in a typical udipsamment of the Niger Delta Basin of Nigeria. *Environmental Monitoring and Assessment*. 2000;6(1):235-249.
 16. Sojину OS, Wang JZ, Sonibare OO, Zeng EY. Polycyclic aromatic hydrocarbons in sediments and soils from oil exploration areas of the Niger Delta, Nigeria. *Journal of Hazardous Materials*. 2010;17(4):641-647.
 17. Liu H, Probst A, Liao B. Metal contamination of soils and crops affected by the Chenzhou lead/zinc mine spill (Hunan, China). *Science of the Total Environment*. 2005;3(39):153-166.
 18. USEPA. Test methods for evaluating solid waste. (5th ed.), method 3031, acid digestion of oils for metals analysis by atomic absorption or ICP spectrometry, United States Office of Solid Waste, EPA 542-F-12-003 Environmental Protection Emergency Response. Washington, DC; 2012.
 19. Khan A, Khan S, Khan MA, Qamar Z, Waqas M. The uptake and bioaccumulation of heavy metals by food plants, their effects on plants nutrients, and associated health risk: A review. *Environmental Science and Pollution Research International*. 2015;22:13772-13799.
 20. Obiajunwa EI, Pelemo DA, Owolabi SA, Fasasi MK, Johnson-Fatokun FO. Characterization of heavy metal pollutants of soils and sediments around a crude-oil production terminal using EDXRF. *Nuclear Instruments and Methods in Physics Research, Section B: Beam Interactions with Materials and Atoms*. 2002;194:61-64.
 21. Xu GL, Liu H, Li MJ, Li ZM, Peng ZH, Zuo LM, He X, Liu WW. *In situ* bioremediation of crude oil contaminated site: A case study in Jiangnan oil field, China. *Bulletin of Environmental Contamination and Toxicology*. 2015;9(5):624–631.
 22. Pegg S, Zabbey N. Oil and water: The Bodo spills and the destruction of traditional livelihood structures in the Niger Delta. *Community Development Journal*. 2013;4(8):391–405.
 23. Omeje K. Oil conflict in Nigeria: Contending issues and perspectives of the local Niger Delta people. *New Political Economy*. 2015;10(6):321–334.
 24. Umukoro N. Governance and environmental inequality in Nigeria: Implications for conflict management strategies in the Niger Delta. *International Journal of Environmental Studies*. 2012;6(9):913–920.
 25. Nwilo PC, Badejo OT. Impacts and management of oil spill pollution along the Nigerian coastal areas. *Adm. Mar. Spaces Int*. 2006;1(19):23-31.
 26. Useh MU, Ikokoh P, Dauda MS, Onwuazor OP, Uzama D. Physico-chemical and bacteriological analysis of sludge and water contaminated by oil spillage in some coastal communities of Akwa Ibom State, Nigeria. *Advances in Applied Sciences*. 2017;2(5):64-68.
 27. US EPA. Sludge sampling and analysis guidance document. EPA's Office of Sediment Regulation and Standards, Washington, DC; 2005.
 28. Useh MU, Useh UJ, Dauda MS. Characterization of environmental samples around an indigenous refinery in Nigeria. *Biochemistry and Molecular Biology*. 2017;2(6):73-79.
 29. Saxena S, Srivastava RK, Samaddar AB. *Environmental analysis -water, soil and air*. 2nd edition, Agro Botanical Publishers (India). 2013;123-148.
 30. American Public Health Association. *Standard methods for the examination of water and wastewater*. APHA, AWWA, WEF/2009, APHA Publication. 20th ed. Washington DC; 2009.
 31. Wang Z, Stout SA. *Standard handbook oil spill environmental forensics: Fingerprinting and Source Identification*. Elsevier/Academic Press; 2016.
 32. Moez B, Houda B, Ridha A, Chafal A. Assessment of heavy metals contamination and their potential toxicity in the surface sediments of Sfax Solar Saltern, Tunisia. *Environmental Earth Science*. 2018;77:27-49.
 33. Birch GF. A scheme for assessing human impacts on coastal aquatic environments using sediments. In: Woodcoffe CD, Furness RA (eds) *Coastal GIS: An integrated approach to Australian coastal issues*. Wollongong University Papers in Center for Maritime Policy, 14, Australia; 2003.
 34. Maurizio B. The importance of enrichment factor (EF) and geoaccumulation index

- (Igeo) to evaluate the soil contamination. *Geology and Geophysics*. 2016;5:1-4.
35. Chen J, Zhou HC, Wang C, Zhu CQ, Tam NF. Short-term enhancement effect of nitrogen addition on microbial degradation and plant uptake of polybrominated diphenyl ethers (PBDEs) in contaminated mangrove soil. *Journal of Hazardous Materials*. 2015;3(8):84-92.
 36. Mandal AJ, Sarma PM, Singh B, Jeyaseelan CP, Channashettar VA. Bioremediation: An environment friendly sustainable biotechnological solution for remediation of petroleum hydrocarbon contaminated waste. *ARPN Journal of Science and Technology*. 2012;2(8):1-12.
 37. Rowland UO, Yusuf OM, Ify LN. Bioremediation of crude oil contaminated soil using organic and inorganic fertilizers. *Journal of Petroleum and Environmental Biotechnology*. 2015;6(1):27-35.
 38. Karami A, Shamsuddin ZH. Bioremediation of heavy metals with several efficiency enhancer methods. *African Journal of Biotechnology*. 2010;9(5):89-98.
 39. Bierkens J, Geerts L. Environmental hazard and risk characterisation of petroleum substances: A guided "walking tour" of petroleum hydrocarbons. *Environ. Int*. 2014;6(6):182-193.
 40. Raji AY, Abejide TS. An assessment of environmental problems associated with oil pollution and gas flaring in the Niger Delta Region Nigeria. *J. Environ. Prot*. 2013;9(6):48-62.
 41. Nathanail CP, Bardos RP, Gillett A, McCaffrey C, Ogden R, Scott D, Nathanail J. International processes for identification and remediation of contaminated land. Land Quality Management Ltd., Nottingham, UK; 2013.
 42. Chorom M, Sharif HS, Mutamedi H. Bioremediation of a crude oil-polluted soil by application of fertilizers. *Iranian Journal of Environmental Health Science and Engineering*. 2010;7(9):319-326.
 43. Towell MG, Bellarby J, Paton GI, Coulon F, Pollard ST, Semple KT. Mineralization of target hydrocarbons in three contaminated soils from former refinery facilities. *Environmental Pollution*. 2011;15(9):515-523.
 44. Valls M, de Lorenzo V. Exploiting the genetic and biochemical capacities of bacteria for the remediation of heavy metal pollution. *FEMS Microbiology Reviews*. 2002;2(6):327-338.
 45. Orji FA, Abiye AI, Dike EN. Laboratory scale bioremediation of petroleum hydrocarbon - polluted mangrove swamps in the Niger Delta using cow dung. *Malaysian Journal of Microbiology*. 2012; 8(4):219-228.
 46. Hou D, Al-Tabbaa A. Sustainability: A new imperative in contaminated land remediation. *Environmental Science Policy*. 2014;3(9):25-34.

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Peer-review history:
The peer review history for this paper can be accessed here:
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