Heavy Metal Toxicity Levels and Ecological Risk Assessment of Petroleum-Based Pollutants in the Sediments of the Soku Oil and Gas Field of Southern, Nigeria

Niveles de toxicidad de metales pesados y evaluación del riesgo ecológico de los contaminantes derivados del petróleo en los sedimentos del campo petrolífero y gasífero de Soku, en el sur de Nigeria

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Artículos

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Abstract

The Soku Gas Plant and associated oil facilities in South-south Nigeria has been a source of continuous discharge of oil spills and other industrial wastes to the ecosystems surrounding it.

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Standard methods were used to analyze the concentrations of heavy metals (Zn, Pb, Ni, Cr and Cd) and PAHs in the sediments. The result of this study revealed that the concentration of both PAHs and heavy metals was within the PEL and TEL guideline values. Five methods of pollution assessment of metals were conducted including the Geo-accumulation Index (I-geo), Contamination Factor (Cf), Pollution Load Index (PLI), Potential Ecological Risk Index (PERI) and Metal Toxicity. The result of CF, CD, and PLI in this study, Cd had the highest and Cr had the lowest CF average values among the five metals studied. The contamination factor in the study area showed higher levels for cadmium and lower levels for chromium in all stations while the calculated PERI for all the sample stations in the study area indicated low potential ecological risk. The potential ecological risk index (PERI) can be ranked in the following order: Station 3 (Pangapingi)> Station 4 (Soku Jetty) > Station 2(Gas plant) > Station 1(Elem Sangama). Spatial distribution of single risk indices (Eir) showed moderate to low risk. The I-geo classes for the study area varied across metals and sites ranging from uncontaminated to moderately contaminated. Clean-up of oil pollution and payment of compensation as required by law and convention was recommended.

Keywords: ecological risks, geo-accumulation, hazard characterization, niger delta, pollution load.

Resumen

La planta de gas Soku y las instalaciones petroleras asociadas en el sur de Nigeria han sido una fuente continua de vertidos de petróleo y otros residuos industriales a los ecosistemas circundantes. Se utilizaron métodos estándar para analizar las concentraciones de metales pesados (Zn, Pb, Ni, Cr y Cd) y HAP en los sedimentos. El resultado de este estudio reveló que la concentración tanto de HAP como de metales pesados se encontraba dentro de los valores de referencia de PEL y TEL. Se llevaron a cabo cinco métodos de evaluación de la contaminación por metales, entre ellos el índice de geoacumulación (I-geo), el factor de contaminación (Cf), el índice de carga contaminante (PLI), el índice de riesgo ecológico potencial (PERI) y la toxicidad de los metales. Los resultados del CF, el CD y el PLI en este estudio mostraron que el Cd tenía los valores medios más altos y el Cr los más bajos entre los cinco metales estudiados. El factor de contaminación en la zona de estudio mostró niveles más altos para el cadmio y más bajos para el cromo en todas las estaciones, mientras que el PERI calculado para todas las estaciones de muestreo de la zona de estudio indicó un riesgo ecológico potencial bajo. El índice de riesgo ecológico potencial (PERI) puede clasificarse en el siguiente orden: Estación 3 (Pangapingi) > Estación 4 (Soku Jetty) > Estación 2 (Planta de gas) > Estación 1 (Elem Sangama). La distribución espacial de los índices de riesgo únicos (Eir) mostró un riesgo de moderado a bajo. Las clases I-geo para el área de estudio variaron según los metales y los sitios, desde no contaminados hasta moderadamente contaminados. Se recomendó la limpieza de la contaminación por hidrocarburos y el pago de indemnizaciones según lo exigido por la ley y los convenios.

Palabras Clave: riesgos ecológicos, geo-acumulación, caracterización de peligros, delta del Níger, carga contaminante.

Introduction

The Niger Delta has been categorized as heavily contaminated with oil residue resulting from oil spillages. Over the years, petroleum-based pollutants such as toxic metals and petroleum hydrocarbons have accumulated in the water, sediment, and soils of the Niger Delta in Nigeria,

becoming a source of concern for environmental authorities and the area's inhabitants. This situation has arisen from frequent oil spills, which now average four per day (Egborge, 1991; NRC, 2003; UNEP, 2011).

The Niger Delta is among the ten most important wetland and marine ecosystems in the world. The oil industries located within this region have contributed immensely to the country's growth and development, a fact that cannot be disputed. However, unsustainable oil exploration activities have resulted in significant damage to the Niger Delta's ecosystem. Studies have shown that the quantity of oil spilled over 50 years is equivalent to 50 Exxon Valdez spills (FME, 2006). The Niger Delta consists of diverse ecosystems, including mangrove swamps, freshwater swamps, and rainforests, and is the largest wetland in Africa. However, due to oil pollution, the area is now characterized by contaminated streams and rivers, forest destruction, and biodiversity loss; in general, it is becoming a vast ecological wasteland (Amadi, Abbey, y Nma, 1996). This situation affects the livelihoods of the indigenous people who depend on ecosystem services for survival.

Oil spillage may result from many factors, such as valve failure, blowouts, human error (negligence by personnel), rupture of pipes, operational failure, and deliberate damage (UNEP, 2011). Hundreds of oil spills occur in Nigeria every year, causing significant harm to the environment, destroying local livelihoods, and placing human health at serious risk (UNEP, 2011). However, the Shell Petroleum Development Company (SPDC) report for the period 2007-2014 indicates that a total of 1,427 oil spill incidents occurred from their facilities in the Niger Delta. In a related report by IUCN/CEESP (2006), it was shown that between 9 and 13 million barrels of oil were spilled into the Niger Delta ecosystem over the past 50 years.

In the Soku area, oil spills from the Shell Nigeria Company facilities occur daily due to equipment failure and human negligence. This situation has been compounded by additional spills, gas explosions, and fires, which have resulted in significant loss of human life and the destruction of hectares of mangrove forests caused by oil theft, illegal bunkering, and artisanal oil refining and transportation activities (Ezekwe, Eludoyin, y Adigwe, 2015). Oil exploration and exploitation began in Soku in 1957 with SPDC, following the earlier discovery in Oloibiri in 1956, and has continued to the present day. The effects of spillages on the ecosystem in the study area have been severe, including damage to and loss of biodiversity, reduction of arable land, diminished availability of drinking water, and blockages of waterways (Omo-Irabor et ál., 2011). The presence of heavy metals in areas affected by oil spills also hampers the biodegradation of the spilled oil, thereby delaying the recovery of such areas (Almeida, Mucha, Teixeira, Burdalo and Almeida, 2013). The health of workers and residents in oil spill areas is often adversely affected by the spilled oil (Gwack et ál., 2010). It is also noteworthy that sensitive ecosystems, such as mangrove forests, may take up to three decades to recover from the effects of spillage, even after necessary cleanup and bioremediation measures have been completed (UNEP, 2011). This is because spilled oil can enter the food chain and settle at the bottom of water bodies, where it contaminates sediments.

According to Mendelssohn et ál. (2010), about 50% of spilled oil evaporates, while others migrate and disperse due to the action of wind and tidal waves. Some oil emulsifies, and a percentage unnoticeably sinks to the riverbed, permeating the bottom sediments. Sediments are a key element of the marine ecosystem. Due to their physicochemical properties, sediments serve as a sink for contaminants and subsequently become a source of recontamination for the ecosystem components to which they are linked. Significant contamination of sediments may lead to species loss (Burton y Statham, 2000). The potential impacts of sediment-related contamination are wide-ranging, with deleterious effects observable throughout the biological continuum—from benthic communities via direct exposure to upper trophic levels (aquatic and terrestrial) through food web contamination (Burton et ál., 2000). The contribution of contaminated sediments to effects on sediment-dwelling organisms (including plants and invertebrates), aquatic-dependent wildlife (amphibians, reptiles, fish, birds, and mammals), and human health has become increasingly apparent in recent years.

Ezekwe and Utong (2017) also noted that “sediments are sinks for contaminants in river ecosystems, and their physico-chemical properties and response to the chemical dynamics of the hydrological system may enhance subsequent contamination of the ecosystem components to which they are linked. Significant contamination of sediments may lead to species and biodiversity losses (Markovic, 2003; Luoma, 1990) and deleterious food chain reactions from benthic communities to upper trophic levels (Burton, 2002), either through direct adverse impacts on bottom fauna or by becoming long-term sources of toxic substances to the environment. They can also impact wildlife and humans through the consumption of food or water or by direct bodily contact. Of critical importance is that these impacts may be present even though the overlying water meets water quality criteria (USEPA, 1992), thereby underscoring the importance of sediment quality analysis in monitoring ecosystem integrity."

With the importance of sediments as sinks and probable sources of recontamination in aquatic or marine systems in mind, it becomes pertinent to study the concentrations of toxic metals and hydrocarbons in the sediments of the Soku oil and gas fields to ascertain their toxicity levels and possible environmental health effects.

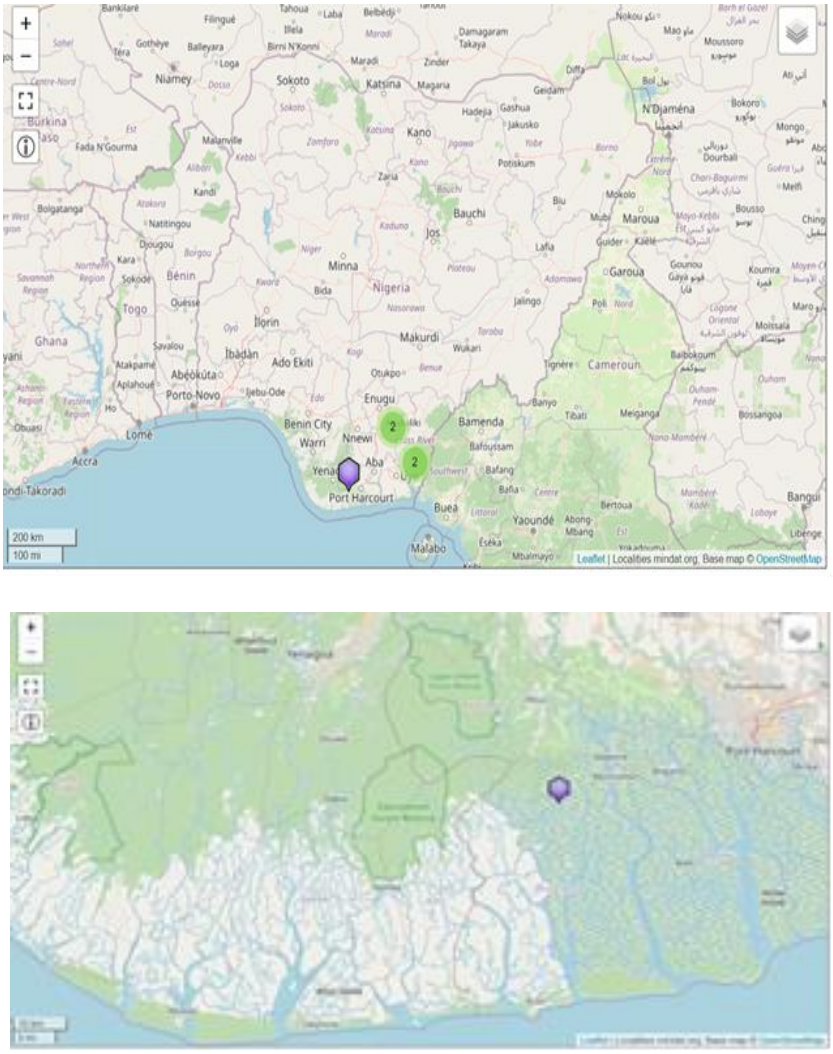
Study Area

According to Ezekwe, Eludoyin, and Adigwe (2015), the Soku community is home to many oil and gas wells operated by the Royal Dutch Shell company, specifically the Shell Petroleum Development Company (SPDC) of Nigeria. This includes three flow stations (Soku, Ekulama I, and Ekulama), the Oil Remediation Development Project (ORD), and the Soku Liquefied Natural Gas Plant (Soku Gas Plant Facility-SPDC) project, which provided 100% of the total gas feedstock to the Bonny LNG terminal before the completion of the Obiafu/Obrikom (Agip) and Obite (Total ELF) gas plants, and 63.7% of the gas feedstock thereafter. The study area is located within latitudes 4° 38' 50”N^{o} and 4° 42' 05”N^{o} and longitudes 6° 35' 45”E^{o} and

6°° 41' 03”E (Figure 1y2). This covers an area of about 50 square kilometers in the Akuku-Toru Local Government Area, Rivers State, in the south-central region of the Niger Delta of Nigeria.

Figure 1

a and b. Map of Nigeria study area (Mindat.org, 2023)



The region has a tropical hot monsoon climate due to its latitudinal position, characterized by very high year-round temperatures and consistently high relative humidity. Heavy rainfall occurs between April and October, ranging from 2,000 mm to 2,500 mm. The relief consists of lowland, with an average elevation of no more than 5 meters above sea level. Geology comprises recent alluvium, primarily consisting of sand but mostly muddy deposits. The soil is typically sandy or sandy loam, underlain by a layer of impervious clay and generally surrounded by tidal estuarine water bodies, including the distributaries of the Sombreiro and Saint Bartholomew rivers. The settlements in the Soku area are small and dispersed, usually

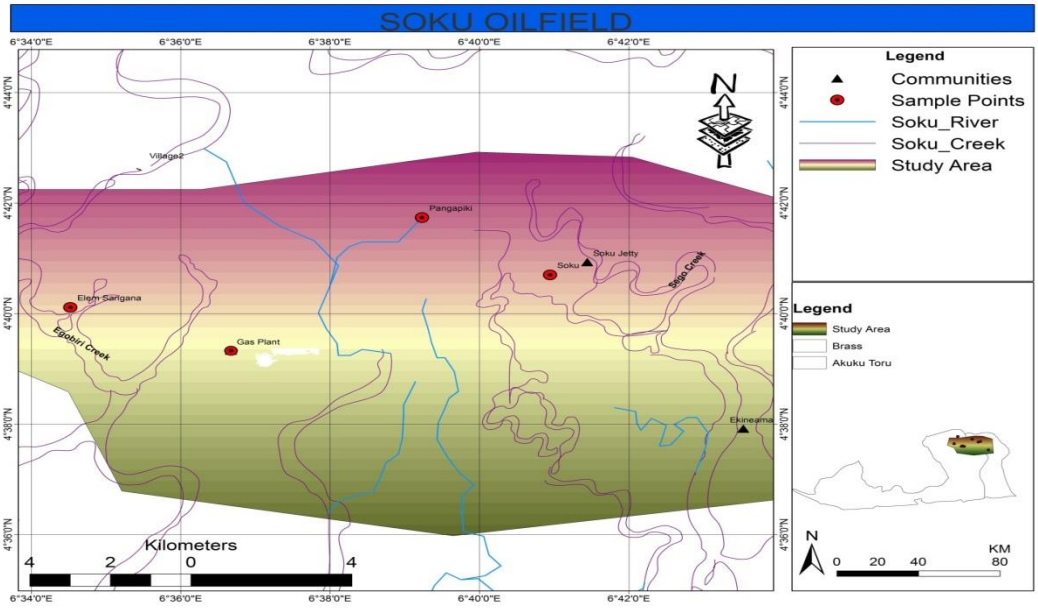
separated by creeks, with local weaving, fishing, and farming as the primary occupations (Ezekwe, Eludoyin, and Adigwe, 2015).

Materials And Methods

A reconnaissance survey of the study area was undertaken in April 2016 with a canoe and assistance from local inhabitants. During this survey, four sample stations were established: Elem-Sangama community, Gas Plant, Pangapiki (control), and Soku Jetty. These locations were selected due to the intense oil spillage observed, which is the focus of this study. The geographical coordinates of each sampling point were recorded using hand-held GPS equipment (GARMIN 76). The coordinates are as follows: Elem-Sangama (E $006^{0}34´.913"$ N $04^{0}40´.379"$), Gas Plant (E 00603^{0} ´ 4.915" N 04040^{o} ´.383"), Pangapiki (E $006039'04^{0}.0"$ N $04041'22^{0}$ .7"), and Soku Jetty (E $006041'01^{0}$ .0" N $04040'46^{0}$ .9").

Figure 2

Sampling Sites



Field observations indicated that the Elem-Sangama community environment on the western side of the Soku Gas Plant is characterized by densely populated mangrove plant species, along with abundant periwinkles, fish, and birds. The mud and surface water exhibited oil sheens and slicks floating freely. In contrast, at the Soku Gas Plant Sampling Site, there were no visible signs of marine life, only a vast expanse of shallow water containing dead and largely decaying mangrove vegetation. At Pangapiki Station, the dense brackish water vegetation was covered with oil slicks. A few faunae, such as juvenile periwinkles, crabs, and mudskippers, were observed in the mangrove mud. Oil sheens and slicks were also seen floating freely on the surface water.

Figure 3
Plate I: *Oil Spill Floating on Water*

Figure 4
Plate II: area of lost mangrove vegetation

At the Soku Jetty sampling site, the mangrove plants were densely populated, although their roots were covered with oil. Marine fauna such as fish, periwinkles, mudskippers, and birds were spotted in the area. Oil sheens and slicks were also found floating freely on the surface of the water.

Method of sample collection and analysis

The methods described in Ezekwe and Utong (2017) were applied in this study. River bottom sediment samples were collected with the aid of a modified Eckman grab bottom sediment sampler from four purposefully selected sites. The sample sites were chosen from four grids that covered most of the study area. Sediment samples were collected using the grab method in triplicates at low tide in June 2013 (rainy season) and November 2013 (dry season) (APHA, 1998). Samples for hydrocarbon analysis were stored in sterilized bottles, while samples for trace metal analysis were stored in polythene bags previously washed in diluted HCl. Samples for organic matter analysis were collected in aluminum foil. All samples were sealed in polyethylene bags and stored in ice-packed plastic coolers (below 4°C) before being transported to the laboratory and analyzed within two days.

Estimation of trace metal content

The sediment samples were allowed to thaw, air-dried at ambient temperature, ground, and sieved through 0.5 mm mesh. Later, 2 g of each sample was digested using a 25 ml mixture of hydrochloric acid (HClO4), nitric acid (HNO3), and sulfuric acid (H2SO4) in a 1:3:1 ratio in a water bath. Ten milliliters of deionized water were added to the digest, which was then decanted into a 50 ml standard flask and brought to the mark with deionized water after rinsing. The Buck Scientific Atomic Absorption Spectrophotometer, Model 200A, equipped with an air-acetylene flame, was used for trace metal analyses. Quality assurance was checked with the standard sediment sample PACS-2 using an intra-run Quality Assurance Standard (1 mg/l, Multi-Element Standard Solution, Fisher Scientific) after every 10 samples (Cantillo and Calder, 1990).

Estimation of total organic carbon (toc)

The Walkley-Black wet chemistry “reference” procedure for the determination of Total Organic Carbon, as described in Schumacher (2002) and applied by Marcus and Ekpete (2014), was used to analyze total organic carbon (TOC) in this study. One gram of dried, sieved sediment was placed into a 250 ml conical flask and digested with 10 ml of 0.5 M K2Cr2O7 and 20 ml of concentrated H2SO4, then swirled and allowed to cool. To address concerns regarding incomplete digestion of organic matter, the sample and extraction solutions were gently boiled at 150 ºC for 30 minutes and then allowed to cool (Walkley y Black, 1934; Tiessen y Moir, 1993). Once cooled (after 20-30 minutes), 100 ml of deionized water was added for dilution, and 3 or 4 drops of ‘Ferroin’ indicator were added before titration with 0.4 N FeSO4 solution (NSW EH, 2015). The results of TOC were reported as a percentage and later converted to dry weight (Table 1) by multiplying the total organic matter content (%) by sediment bulk density (1.61 g/cm³) and the depth (20 cm) of sampling (Pluske et ál., 2016).

Estimation of hydrocarbon (PAHs)

Samples for hydrocarbon analysis were weighed to obtain wet weight, then sun-dried, ground to a powdery form, and sieved using a 1.0 mm sieve. The sieved samples were stored in well-labeled smaller plastic containers with covers, from which samples were withdrawn for analysis. Five grams of each dry powdery sample were weighed out and placed in 250 ml beakers. To this, 30 ml of xylene was added; the beaker was then swirled or shaken for about 5 minutes and allowed to settle. The mixture was later filtered into a clean 100 ml standard flask through Whatman filter paper containing about 2 g of anhydrous sodium sulfate on cotton wool. This process was repeated three times and was subsequently made up to the 100 ml mark with xylene. The absorbance of the filtrate was measured at 340 nm using a Hach DR 2800 Spectrophotometer. The corresponding concentrations of total hydrocarbon (THC) content were then obtained from the calibration curve and calculated on a dry weight basis. The same procedure was applied to the analysis for total petroleum hydrocarbon (TPH); however, after the extraction, the filtrate was treated with silica gel to remove non-petroleum hydrocarbons and re-filtered. The readings were obtained in the same manner as those for THC, and the final value was calculated as usual (Howard, Gabriel and Horsfall, 2009). Calibration of the spectrophotometer (Hach DR 2800) was carried out before each analysis using diluents from a stock solution of 1 ml of crude oil in 100 ml of xylene at 340 nm, in accordance with ASTM (2003) and Howard et ál. (2009).

Ecological Risk Assessment Methods

described in Ezekwe and Utong (2015) were applied in this study. Sampled sites were correlated with each other to assess relationships and differences, while contaminants found in sediments from the above analysis were discussed against the backdrop of Sediment Quality Standards, which are guidelines for relating chemical concentrations in sediment to their potential biological effects (Bay et ál., 2012). In this study, five methods of pollution assessment of metals were used, including the Geo-accumulation Index (I-geo) (Muller, 1969), Contamination Factor (CF), Pollution Load Index (PLI), Hakanson Potential Ecological Risk Index (Hakanson, 1980), and Metal Toxicity Index, as described in Ezekwe and Utong (2015). The background values of Ni, Cr, Cd, Pb, and Zn were 68 mg/kg, 90 mg/kg, 0.22 mg/kg, 60 mg/kg (Li et ál., 2012), and 120 mg/kg, respectively (Rodrigues and Formos, 2006).

Geo-Accumulation Index (I-Geo)

The Geo-accumulation index is a quantitative measure of the degree of pollution in aquatic sediments (Singh, Singh, y Mohan, 2005). It consists of seven classes ranging from practically uncontaminated (0) to extremely contaminated (6), as shown in Table 1. The Geo-accumulation Index (I-geo) is defined by the following equation:

$$Igeo = \log_2 (C_n/K \times B_n) \quad (1)$$

Where:

C_n is the concentration of metal n, and B_n is the background concentration of metal n. The factor K is the background matrix correction factor due to lithospheric effects, which is usually defined as 1.5 (Muller, 1969). The classification of the geo-accumulation index is presented in Table 1.

Table 1

Muller Classification for Geo-Accumulation Index

I-geo	Class	Pollution status
>5	6	Extremely contaminated
4-5	5	Heavily to extremely contaminated
3-4	4	Heavily contaminated
2-3	3	Moderately to heavily contaminated
1-2	2	Moderately polluted
0-1	1	Uncontaminated to moderately contaminated
0	0	Practically uncontaminated

Contamination Factor (CF) and Pollution Load Index (PLI)

Pollution severity and its variation across different sites are determined using the Pollution Load Index (PLI). This is a quick tool for comparing the pollution status of various locations (Adebowale, Agunbide, y Olu-Owolabi, 2009). The PLI is derived from Contamination Factors (CF), which are calculated as the quotient obtained by dividing the concentration of each metal by a reference value. The PLI is defined as the nth root of the product of the concentrations (CF of $_{metals}$). The Pollution Load Index was developed by Tomlinson, Wilson, Harris, and Jeffeney (1980) and is expressed as follows:

$$CF = C\ metal / C\ background\ value \quad \text{(2)}$$

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \ldots\ldots CFn)^{1/n} \quad \text{(3)}$$

Where,

CF = contamination factor

n = number of metals

C metal = metal concentration in polluted sediments

C background value = background value of that metal

Values of PLI > 1 imply that heavy metal pollution exists. Otherwise, if PLI <1, there is no heavy metal pollution (Tomlinson et ál., 1980).

Potential Ecological Risk Index (PERI)

The Potential Ecological Risk Index was developed by Hankanson (1980) and integrates the concentration of heavy metals with ecological effects, environmental effects, and toxicology. It is used to assess heavy metal pollution and ecological risk in sedimentology. The Hankanson Potential Ecological Risk Index (PERI) is defined as follows:

$$C_f^i = \frac{C_i}{C_n^i} \quad \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

$$E_r^i = T_r^i C_f^i \quad \ldots\ldots\ldots\ldots\ldots\ldots (5)$$

$$RI = \sum_i^m E\binom{i}{r} \quad \ldots\ldots\ldots\ldots\ldots\ldots (6)$$

Where:

C_i and C^i_n are the concentrations of metals examined in sediment samples and the geochemical background values of metals, respectively.

C^i_f is the monomial contamination factors.

T^i_r is the toxic-response factor for a given substance, e.g. Ni=5, Cr=2, Cd=30, Pb=5 and Zn=1.

RI is the sum of all risk factors for heavy metals in sediments. The first module of PERI corresponds to the estimate of the degree of contamination (C_D). The C_D is expressed as the sum of the contamination factor for each metal (Cf^i):

$$C_D = \Sigma Cf \ldots\ldots\ldots\ldots\ldots\ldots (7)$$

The relation between evaluation indices and the pollution degree and potential ecological risk are shown in Table 2.

Table 2.

Corresponding relationships between Evaluation Indices, Pollution Degree and Potential Ecological Risks.

C^i_r	Monomial Contamination Factor	E^i_r	Monomial potential ecological risk factor	RI	Sum of all risk factors	Degree of contamination	Description
>1	Low	<40	Low	<150	Low	C_D<8	Low
1-3	Moderate	40-80	Moderate	150-300	Moderate	8≤C_D<16	Moderate
3-6	High	80-160	Moderate to high	300-600	High	16≤C_D<32	Considerable

≥6	Very High	160-320	High	≥600	Very High	C_D≥32	Very high
		≥320	Very High				

Result and discussion

Heavy Metals in Sediment

The concentration of heavy metals and hydrocarbons in the sediments of the study area is shown in Table 3. It presents the presence of heavy metals such as nickel (Ni), chromium (Cr), cadmium (Cd), lead (Pb), and zinc (Zn), as well as total organic carbon (TOC) and polycyclic aromatic hydrocarbons (PAHs) in the sediment of the study area.

Table 3.
The Concentration of Heavy Metals and Hydrocarbons in Sediment

Sample Stations	**TOC (%)**	**Nickel (Ni) mg/kg**	**Chromium (Cr) mg/kg**	**Cadmium (Cd) mg/kg**	**Lead (Pb) mg/kg**	**Zinc (Zn) mg/kg**	**PAH (mg/kg)**
Elem— sangama community	0.507	<0.001	<0.001	0.04	2.30	5.64	0.021
Gas plant	1.092	1.39	<0.001	0.09	3.17	5.18	0.053
Pangapiki	2.691	6.00	4.43	0.38	9.31	17.50	0.033
Soku Jetty	2.840	5.60	4.70	0.24	6.74	20.35	0.030
Average	1.78	3.25	2.28	0.19	5.38	12.17	0.03
STANDARDS (ug/g) After, Pazi, 2011							
Moderately polluted		20-50	25-75	6	40-60	90-200	4
Heavily polluted		>50	>75	>6	>60	>200	>45 (Long and Morgan, 1990)

The concentrations of heavy metals and PAHs in the sediments of the study area, therefore, appeared to be low and safe according to USEPA and NOAA recommendations, as reported by Pazi (2011) and Long and Morgan (1990). The concentrations are also within safe limits compared to those in other aquatic environments, especially in Korea, as reported by Moon et ál. (2007). The sediment quality guidelines that reflect Threshold Effects Concentrations (TECs)—that is, concentrations below which harmful effects are unlikely to be observed—are shown in Table 4. The concentrations of heavy metals and hydrocarbons in the study area, along with the Sediment Quality Guidelines that reflect Probable Effects Concentrations (PECs)—i.e., concentrations above which harmful effects are likely to be

observed—are shown in Table 5. The metal concentrations in the sediments from all the sample stations, as shown in Table 4.1, ranged as follows: Ni, 0.001-6.00 mg/kg; Cr, 0.001-4.70 mg/kg; Cd, 0.04-0.38 mg/kg; Pb, 2.30-9.31 mg/kg; and Zn, 5.18-20.35 mg/kg. The average content of the metals studied was as follows: Ni, 3.25 mg/kg; Cr, 2.28 mg/kg; Cd, 0.19 mg/kg; Pb, 5.38 mg/kg; and Zn, 12.17 mg/kg.

Table 4

Threshold Effect Concentrations (TECs)

Metal (Mg/Kg)	Elem-Sangama	Gas Plant	Pangapiki	Soku Jetty	Dutch Standards	Canadian Guideline TEL	USEPA GUIDELINES					
							TEL	LEL	MET	ERL	TEL-HA 28	TEC
TOC	0.507	1.092	2.691	2.840	NG	NG	NG	NG	NG	NG	NG	NG
Ni	<0.001	1.39	6.00	5.60	35	15.9	18	16	35	30	20	22.7
Cr	<0.001	<0.001	4.43	4.70	100	52.3	37.3	26	55	80	36	43.4
Cd	0.04	0.09	0.38	0.24	0.8	0.7	0.596	0.6	0.9	5	0.58	0.99
Pb	2.30	3.17	9.31	6.74	85	30.2	35	31	42	35	37	35.8
Zn	5.64	5.18	17.50	20.35	140	124	123	120	150	120	98	121
PAH	0.021	0.053	0.033	0.030	1	NG	87	1796	1800	350	2114	290

All the heavy metals in the bottom-sediment samples from this study did not exceed the respective Threshold Effect Concentrations (TEC) and Probable Effect Concentrations (PEC), which, according to the USEPA (1998), are valued in the range where toxic effects can occur in both aquatic life and humans, as shown in Tables 4 and 5.

Table 5

Probable Effect Concentrations (PECs)

Mg/kg Element	Elem-Sangama	Gas Plant	Pangapiki	Soku Jetty	Dutch Standard	Canadian Guideline PEL	USEPA GUIDELINES					
							PEL	SEL	TET	ERM	PEL-HA 28	PEC
TOC	0.507	1.092	2.691	2.840	NG	NG	NG	NG	NG	NG	NG	NG
Ni	<0.001	1.39	6.00	5.60	45	42.8	36	75	61	50	33	48.6
Cr	<0.001	<0.001	4.43	4.70	380	160	90	110	100	145	120	111
Cd	0.04	0.09	0.38	0.24	7.5	4.2	3.53	10	3	9	3.2	4.98
Pb	2.30	3.17	9.31	6.74	530	112	91.3	250	170	110	82	128

Zn	5.64	5.18	17.50	20.35	720	271	315	820	540	270	540	459
PAH	0.021	0.053	0.033	0.030	10	NG	840	10230	10230	2358	2114	10000

The mean metal concentrations can be arranged in the following order: Zn > Pb > Ni > Cr > Cd. Zinc had the highest concentration, while cadmium had the lowest concentration in the study area. Below is a graphical representation of the concentrations of heavy metals and hydrocarbons in the sediments of the study area.

Polycyclic Aromatic Hydrocarbon (PAHs) In Sediment

The hydrocarbon concentration and total organic compound (TOC) in the sediments are presented in Table 2. The TOC ranged from 0.507% to 2.840%, while the PAH values ranged from 0.21 mg/kg to 0.053 mg/kg, with an average concentration of 0.03 mg/kg. The PAH concentration was highest in the gas plant area and lowest in Elem-Sangama. The PAH values for the study area did not exceed the respective Threshold Effect Concentration (TEC) and Probable Effect Concentration (PEC), which, according to the USEPA (1998), are values in the range where toxic effects can occur in both aquatic life and humans, as shown in Tables 4 and 5.

Ecological and health risk assessment

Sediment Pollution Indices

In this study, five methods of ecological risk assessment for hydrocarbons and metals were conducted: the Geo-accumulation Index (I-geo), Contamination Factor (CF), Pollution Load Index (PLI), Hakanson Potential Ecological Risk Index (PERI), and Metal Toxicity Index.

Contamination Factor and Pollution Load Index

The Contamination Factor, Degree of Contamination, and Pollution Load Index for the heavy metals in the sediments of the study area are presented in Table 6. The calculations for metals are shown below.

$$PLI = (Cf_1 \times Cf_2 \times Cf_3 \times \ldots Cfn)^{1/n}$$

Elem-Sangama Community

$$PLI = (0.038 \times 0.00001 \times 0.047 \times 0.182 \times 0.000011)^{1/5}$$

$$= 0.002.$$

Table 6

Contamination Factor and Pollution Load Index for Metals

Sample Stations	CF, Ni	CF, Cr	CF, Cd	CF, Pb	CF, Zn	Degree of Contamination C_D	PLI INDEX
Elem-sangama	0.00001	0.000011	0.182	0.038	0.047	0.267	0.002

Gas Plant	0.02	0.000011	0.409	0.053	0.043	0.523	0.012
Pangapiki	0.088	0.049	1.727	0.155	0.146	2.165	0.176
Soku Jetty	0.082	0.052	1.091	0.112	0.170	1.507	0.155
Average	0.048	0.025	0.852	0.090	0.102	1.116	0.086

In this study, Cd had the highest and Cr had the lowest CF average values among the five metals studied. The contamination factors in the study are arranged as follows:

Elem-Sangama community = Cr < Ni <Pb< Zn < Cd

Gas Plant = Cr < Ni < Zn <Pb< Cd

Pangapiki = Cr < Ni < Zn <Pb< Cd

Soku Jetty = Cr < Ni <Pb< Zn< Cd

The CD values for the degree of contamination were low at all the sample stations. The degree of contamination followed the order of site 3 (Pangapiki) > site 4 (Soku Jetty) > site 2 (Gas Plant) > site 1 (Elem-Sangama).

The severity of pollution and its variation among the sample stations were determined using the pollution load index (PLI). The PLI values ranged from 0.002 to 0.176 (see Table 6). According to Tomlinson et ál. (1980), the mean PLI value of 0.086 indicates that there is no heavy metal pollution in the study area. The results showed that all sample stations were not polluted by the heavy metals investigated. The PLI followed the order of site 3 (Pangapiki) > site 4 (Soku Jetty) > site 2 (Gas Plant) > site 1 (Elem-sangama).

Geo-Accumulation Index (I-geo)

The Geo-accumulation Index for heavy metal in the study area is presented in Table 7. The calculation for the I-geo is shown below.

$I\text{-geo} = \log_2 (C_n/k \times B_n)$

Elem-Sangama Community

I-geo (Ni) = 0.3 (0.00099/1.5 x 68) = 0.3 (0.00099/102) =0.000003

I-geo (Cr) = 0.3 (0.00099/1.5 x 90) = 0.3 (0.00099/135) =0.000002

I-geo (Cd) = 0.3 (0.04/1.5 x 0.22) = 0.3 (0.04/0.33) =0.036

I-geo (Pb) = 0.3 (2.30/1.5 x 60) = 0.3 (2.30/90) =0.008

I-geo (Zn) = 0.3 (5.64/1.5 x 120) = 0.3 (5.64/180) =0.0094

Table 7

Geo-accumulation Index (I-geo) for studying heavy metals

Sample Stations	I-geo Ni	I-geo Cr	I-geo Cd	I-geo Pb	I-geo Zn
Elem-sangama community	0.000003	0.000002	0.036	0.008	0.0094
Gas Plant	0.004	0.000002	0.082	0.011	0.0086
Pangapiki	0.016	0.011	0.218	0.022	0.034
Soku Jetty	0.018	0.0098	0.345	0.031	0.029

The I-geo classes for the sediments varied from metal to metal and site to site. The heavy metals investigated, which include Ni, Cr, Cd, Pb, and Zn, in all sample stations in the study area remained in class one (uncontaminated to moderately contaminated), as shown in the classification of the geo-accumulation index (Muller, 1969), presented in Table 1. The results of the geo-accumulation index indicate that the study area is moderately contaminated with these hazardous heavy metals, which may be derived from oil exploration and exploitation activities in the region.

Potential Ecological Risk Index (PERI)

Suggested by Hakanson (1980), integrates the concentration of heavy metals with ecological effects, environmental effects, and toxicology. It is used to assess heavy metal pollution and ecological risk in sedimentology. The Potential Ecological Risk Index for the study area is presented in Table 8. The calculations for the Potential Ecological Risk Index and the spatial distribution of single risk indices (E^i_r) for the study area are shown below.

Calculated PERI

$CD = \Sigma Cf$

$Cf^I = C^i/C_n^i$

$RI = \Sigma E_r^i$ where $E_r^i = T_r^i \, . \, Cf^i$

Elem–Sangama Community

Tri :Pb =5, Ni = 5, Zn =1, Cd = 30, Cr = 2

Ci : Pb = 2.30, Ni =0.00099, Zn = 5.64, Cd = 0.04, Cr = 0.00099

C_n^i : Pb =60,Ni = 68,Zn = 120, Cd =0.22, Cr = 90

Cf :Pb = 0.038, Ni = 0.00001, Zn = 0.047, Cd = 0182, Cr =0.000011

CD : 0.267

Eri : Pb = 0.19, Ni = 0.00005, Zn = 0.047, Cd = 5.46, Cr = 0.000022

RI: 5.697

Table 8

Evaluation results of bio-available heavy metal and Potential Ecological Risk Index (PERI)

Sample Stations	E^i_r N_i	E^i_r Cr	E^i_r Cd	E^i_rPb	E^i_r Zn	PERI
Elem-Sangama Community	0.00005	0.000022	5.46	0.19	0.047	5.694
Gas Plant	0.1	0.000022	12.27	0.265	0.043	12.678
Pangapiki	0.44	0.098	51.81	0.775	0.146	53.269
Soku Jetty	0.41	0.104	32.73	0.56	0.170	33.974
Average	0.238	0.051	25.568	0.448	0.102	26.405

distribution of single risk indices (E^i_r) is shown in Table 8. It was found that the single risk indices of heavy metals were ranked in the order of Cd > Pb > Ni > Zn > Cr. The Eir^i of Cd at station 3 (Pangapiki) was 51.81, indicating moderate risk, while at all the sample stations, the E^i_r of all the investigated heavy metals indicated low risk. The average ecological risk (E^i_r) of Ni, Cr, Cd, Pb, and Zn are 0.238, 0.051, 25.568, 0.448, and 0.102, respectively, indicating that all the investigated heavy metals posed a low ecological risk to the local ecosystem (Table 2).

To quantify the overall potential ecological risk of heavy metals in sediments, the values of the Potential Ecological Risk Index (PERI) are presented in Table 8. The values from the four sample stations ranged from 5.697 to 53.269, with an average of 26.405. The highest and lowest PERI values were observed at Pangapiki and Soku Jetty, respectively. The calculated PERI for all sample stations in the study area indicated a low potential ecological risk. The potential ecological risk index (PERI) can be ranked in the following order: Pangapiki > Soku Jetty > Gas Plant > Elem-sangama. Therefore, in accordance with the ecological risk indices used for this study, the bottom sediments collected from the study area demonstrate a low ecological risk from heavy metals to the aquatic ecosystem.

Potential Metal Toxicity

The results from the sediment contaminant toxicity levels on aquatic life in the study area are presented in Tables 9-13. The metal toxicity index was evaluated through an indirect estimate of bioavailability based on the concentration of simultaneously extracted metals (SEM). This was accomplished using the following equations and molar masses. According to the Ohio Environmental Protection Agency (2010), metal toxicity is assessed through an indirect estimate of bioavailability based on the concentrations of Simultaneously Extracted Metals (SEM). The first step in evaluating metal toxicity is to determine the concentration of each SEM in µmol. This is done using the following equation and molar masses:

$$\frac{\mathbf{x\mu g}}{\mathbf{y\mu g/\mu mol}} = z \quad \text{..... Equation 10}$$

Where x is the metal concentration, y is the molar mass, and z is the amount of metal in

micromoles and the sum total of moles are given from equation 11 and reported in the following tables:

$$\sum[SEM] = SEM\ Ni + SEM\ Cr + SEM\ Cd + SEM\ Pb + SEM\ Zn \quad \text{..... Equation 11}$$

Table 9

Metal Toxicity for Elem-Sangama Community

Metal	Conc. (mg/kg)	Conc. (µg/kg)	Molar mass	SEM (µmol/kg)
Nickel (Ni)	0.00099	0.99	58.693	0.017
Chromium (Cr)	0.00099	0.99	51.996	0.019
Cadmium (Cd)	0.04	40	112.41	0.356
Lead (Pb)	2.30	2300	207.2	11.10
Zinc (Zn)	5.64	5640	65.38	86.27

Σ (SEM) = 97.762 µmol/kg

AVS = 1 µmol/g

FOC =TOC/100 =0.507/100 = 0.0051

(ΣSEM-AVS)/Foc = 18972.94 µmol/goc

Table 10

Metal Toxicity for the SokuGas Plant

Metal	Conc. (mg/kg)	Conc. (µg/kg)	Molar mass	SEM (µmol/kg)
Nickel (Ni)	1.39	1390	58.693	23.68
Chromium (Cr)	0.00099	0.99	51.996	0.019
Cadmium (Cd)	0.09	90	112.41	0.801
Lead (Pb)	3.17	3170	207.2	15.30
Zinc (Zn)	5.18	5180	65.38	79.23

Σ (SEM) =119.03 µmol/kg

AVS = 1 µmol/g

FOC =TOC/100 =1.092/100 = 0.0109

(ΣSEM-AVS)/FOS = 10828.44 µmol/goc

Table 11

Metal Toxicity for Pangapiki

Metal	Conc. (mg/kg)	Conc. (µg/kg)	Molar mass	SEM (µmol/kg)
Nickel (Ni)	6.00	6000	58.693	102.23
Chromium (Cr)	4.43	4430	51.996	85.20
Cadmium (Cd)	0.38	380	112.41	3.38
Lead (Pb)	9.31	9310	207.2	44.93
Zinc (Zn)	17.50	17500	65.38	267.67

Σ (SEM) =503.41 µmol/kg

AVS = 1 µmol/g

FOC =TOC/100 =2691/100 = 0.02691

(ΣSEM-AVS)/FOS = 18670.01 µmol/goc

Table 12

Metal Toxicity for the Soku Jetty

Metal	Conc. (mg/kg)	Conc. (µg/kg)	Molar mass	SEM (µmol/kg)
Nickel (Ni)	5.60	5600	58.693	95.412
Chromium (Cr)	4.70	4700	51.996	90.392
Cadmium (Cd)	0.24	240	112.41	2.135
Lead (Pb)	6.74	6740	207.2	32.529
Zinc (Zn)	20.35	20350	65.38	311.26

Σ (SEM) =531.728 µmol/kg

AVS = 1 µmol/g

FOC =TOC/100 =2.840/100 = 0.0284

(ΣSEM-AVS)/FOS = 18687.61 µmol/goc

Table 13

Simultaneously extracted metals molar calculations for the study area

SAMPLE STATIONS	Σ(SEM) (µmol/kg)	AVS (µmol/g)	Foc	(Σ SEM –AVS)/Foc ($\mu mol/g_{oc}$)
Elem-Sagama community	97.762	1	0.0051	18972.94

Gas plant	119.03	1	0.0109	10828.44
Pagapiki	503.41	1	0.02691	18670.01
Soku Jetty	531.728	1	0.0284	18687.61

According to the USEPA (2008), when $(\Sigma SEM\text{-}AVS)/F_{OC}$ is less than 130 mols/$g_{oc,}$ there is little to no risk to aquatic life. When $(\Sigma SEM\text{-}AVS)/F_{OC}$ is between 130 and 3000 mols/$g_{oc,}$ further testing and/or additional information is needed to determine the risk to aquatic life. When $(\Sigma SEM\text{-}AVS)/F_{OC}$ is greater than 3000 µmols/g_{oc}, there is a likely risk of toxicity to aquatic life. The metal toxicity in the different sample stations is 18,972.94 mol/g_{oc}, 10,828.44 mol/g_{oc}, 18,670.01 mol/g_{oc}, and 18,687.61 µmol/g_{oc}, respectively. The results indicate that there is a likely risk of toxicity to aquatic life at all the sample stations in the study area. The results can be ranked in the following order: Elem-sangama > Soku Jetty > Pangapiki > Soku Gas Plant. These findings further confirm that there is a likely risk of toxicity to aquatic life at all the sample stations in the study area.

Discussions

In tropical environments, mangrove swamps are among the most important types of coastal wetlands. These ecosystems straddle terrestrial and marine environments, and their diverse habitats support an extensive array of organisms. One of the most significant resources that these ecosystems provide to local populations is food in the form of fish and shellfish. Currently, one of the more subtle factors responsible for the degradation of mangrove ecosystems is pollution from chemical contaminants such as heavy metals and polycyclic aromatic hydrocarbons (PAHs) (Ikwuobodo, 2014). Hydrocarbons and heavy metals are highly toxic to human health. The results from our study indicated the presence of hydrocarbons and heavy metals in the sediments of the study area, including nickel (Ni), chromium (Cr), cadmium (Cd), lead (Pb), and zinc (Zn).

Exposure to nickel causes irritation of the respiratory tract, pulmonary and gastrointestinal toxicity, diffuse intestinal pneumonitis, cerebral edema, and even death. It also causes cancer outside the lungs and nasal cavity. Lead (Pb) has serious consequences for the health of children. At high levels of exposure, lead affects the brain and central nervous system, leading to coma, convulsions, and even death. Exposure to high levels of lead may cause anemia, weakness, kidney and brain damage, and even death in adults (Ndubuisi y Asia, 2007).

The acute (short-term) effects of cadmium in humans through inhalation exposure primarily affect the lungs, leading to conditions such as pulmonary irritation. Chronic (long-term) inhalation or oral exposure to cadmium results in a buildup of cadmium in the kidneys, which can cause kidney disease. Chronic human exposure to high levels of chromium (VI) through inhalation or oral routes may produce effects on the liver, kidneys, intestines, immune

system, and possibly the blood (Ikwuobodo, 2014). Zinc is an essential element that is abundant in rocks and ores and is also present in natural waters, albeit as a minor constituent. It plays a crucial role in human nutrition, with food serving as the primary source of zinc for the body. While zinc may be toxic to aquatic organisms, the degree of toxicity varies significantly depending on water quality characteristics and the species being considered (Ndubuisi y Asia, 2007).

Upon entering mangrove ecosystems, chemical contaminants may partition into the sediment, aquatic, or biotic environment phases. In the sediment phase, these contaminants are capable of exerting negative effects on sediment-dwelling organisms. When chemical contaminants bioaccumulate in organisms residing in mangrove ecosystems, they may have deleterious effects on the organisms themselves. In cases where these organisms are harvested for human consumption, the contaminants may threaten the health of human consumers. Overall, pollutants in mangrove ecosystems may negatively impact on the health of organisms living in these environments, as well as the health of humans (Xia et ál., 2010).

Human health risk assessment quantifies the potential risks of exposure to sediment. There exists a potential exposure pathway between humans and the contaminated sediments through trophic levels and the food chain. The bioavailability of contaminants affects their toxicity to aquatic life, resulting in bioaccumulation issues via fish and water consumption (Iwuchukwu, 2006). Some of the exposure pathways in the human health risk assessment include the consumption of resident fish and shellfish taken from the study area, infant consumption of human breast milk from mothers who are exposed to contaminants from the study area, and direct contact with in-water or shoreline sediment (USEPA, 2013).

The concentrations of heavy metals in sediments vary according to the rate of particle sedimentation, the rate of heavy metal deposition, the particle size, and the presence or absence of organic matter in the sediments (Adel et ál., 2011). Although sediment grain size analysis was not considered in this study, the concentrations of metals in the sediment were like those reported in the IUCN-NDP (2013). In this study, the concentrations of hydrocarbons and heavy metals were within the permissible limits specified in the stipulated Sediment Quality Guidelines. The PAH and TOC values for this study ranged from 0.21 to 0.053 mg/kg and 0.507 to 2.840%, respectively, which were below those reported in the Soku Biophysical Report (IUCN-NDP, 2013) and those found in the sediment of the Oturuba stream in Andoni, Rivers State, Nigeria (Ezekwe et ál., 2017).

In this study, Cd had the highest Pollution Load Index (PLI), while Cr had the lowest average contamination factor values. The results indicate the presence of heavy metals and hydrocarbon concentrations in the sediments that are within the permissible limits of Sediment Quality Guidelines; however, there is a high level of risk of toxicity to aquatic life, which may also affect humans via the food chain.

Conclusion and recommendation

The human risk assessment evaluates the potential risks associated with exposure to sediments. The results from the analysis indicate the presence of nickel, chromium, cadmium, lead, and zinc in the sediments of the study area, all of which are highly toxic to human health. There exists a potential exposure pathway between humans and the sediment through the food chain, specifically via fish consumption. This poses high risk levels for illnesses such as kidney diseases, cancer, and even death in humans. The concentrations of heavy metals and hydrocarbons from this study suggest that the level of pollution observed visually in the study area is not reflected in the sediment accumulation. This observation warrants further research.

The results of this study indicate that key findings include the presence of heavy metals and hydrocarbon concentrations in the sediments. These contaminant concentrations cause moderate pollution and pose a low potential ecological risk to the study area, although they present a very high toxicity level of risk to both aquatic life and humans. Therefore, while there may be low health risks to humans and the general ecosystem, fish may be exposed to serious environmental health issues through the bioaccumulation of metals. This finding confirms the concerns raised by Xia et ál. (2010) that heavy metals and hydrocarbons at concentrations below permissible limits can still pose risks of contamination to both aquatic life and humans due to the dynamics of ecosystem processes. This situation highlights the need for a review of sediment risk assessment methods, given the discrepancies and variability in results from different risk assessment approaches.

On the strength of the findings of this study, we hereby advocate for the intervention of the Federal Environmental Protection Agency (FEPA), the National Oil Spill Detection and Response Agency (NOSDRA), and the National Environmental Standards Regulatory Enforcement Agency (NESREA). To restore the environment of the Soku area, there should be a technical committee comprising representatives from both the companies and the government that will conduct routine checks on the companies and their activities.

There should be a compensation payment and a clean-up exercise for the areas affected by oil pollution, as outlined in the Environmental Agency Act No. 47 of 1992. The National Orientation Agency (NOA) should conduct a campaign against sabotage to raise awareness among the public about the dangers of undermining companies' efforts to protect the environment.

References

Adebowale, K. O., Agunbide, F. O. & Olu-Owolabi, B. (2009). Trace metal concentration, site variations and partitioning pattern in water and bottom sediments from coastal area: A case study of Ondo Coast, Nigeria. *Environmental Research Journal, 3*(2), 46-59.

Adel, M. R., Yaaroub, F. A., Abd-Al-Husain, N. A. & Mustafa, N. (2011). Using pollution load index (PLI) and geoaccumulation index (I-geo) for the assessment of heavy metals pollution in Tigris River sediment in

Baghdad region. *Department of Biology, College of Science, University of Baghdad, Ministry of Science and Technology*.

Alaska Department of Environmental Conservation (ADEC). (2011). *Total maximum daily loads (TMDLs) for petroleum hydrocarbons in the waters of Skagway harbor in Skagway, Alaska*. ADEC.

Almeida, R., Mucha, A. P., Teixeira, C., Burdalo, A. A. & Almeida, C. M. (2013). Biodegradation of petroleum hydrocarbons in estuarine sediment metal influences. *Biodegradation, 24*(1), 111-123.

Amadi, A., Abbey, S. D. & Nma, A. (1996). Chronic effects of oil spill on soil properties and microflora of a rain forest ecosystem in Nigeria. *Water, Air, and Soil Pollution, 86*(1-4), 1-11.

Amnesty International Nigeria. (2015). *Exploitation of natural resources, oil spill investigation in the Niger Delta*. https://www.amnesty.org/

Andersen, M. C., Thompson, B. & Boykin, K. (2004). Spatial risk assessment across large landscapes with varied land use: Lessons from a conservation assessment of military lands. *Risk Analysis, 24*, 1231-1242.

Anifowose, B. (2008). Assessing the impact of oil and gas transport on Nigerian environment. *U21 Post-graduate Research Conference Proceedings, 1*. University of Birmingham, UK.

American Public Health Association (APHA). (1998). *Standard methods for the examination of water and wastewater* (20.ª ed.). APHA-AWNA-WPCF.

AS/NZS. (2004a). *Risk management* (AS/NZS 4360:2004). Standards Australia International.

AS/NZS. (2004b). *Risk management guidelines: Comparison to AS/NZS 4360:2004* (HB 436:2004). Standards Australia International.

Bartell, S. M., Gardner, R. H. & O'Neill, R. V. (1992). *Ecological risk estimation*. Lewis Publishers.

Bay, S. M., Ritter, K. J., Vidal-Dorsch, D. E. & Field, L. J. (2012). Comparison of national and regional sediment quality guidelines for classifying sediment toxicity in California. *Integrated Environmental Assessment and Management, 4*, 597-609. https://doi.org/10.1002/team.n1330

Briggs, K. T., Yoshida, S. H. & Gershwin, M. E. (1996). The influence of petrochemicals and stress on the immune system of sea birds. *Regulatory Toxicology and Pharmacology, 23*, 145-155.

Burgman, M. A. (2005). *Risks and decisions for conservation and environmental management*. Cambridge University Press.

Burton, J. D. & Statham, P. J. (2000). Trade metals in seawater. En R. W. Furness y P. S. Rainbow (Eds.), *Heavy metals in the marine environment* (pp. 5-25). CRC Press.

Canadian Council of Ministers of the Environment. (2002). *Canadian sediment quality guidelines for the protection of aquatic life summary tables updated in Canadian environmental quality guidelines, 1999*. Canadian Council of Ministers of the Environment.

Cantilo, R. A. & Calder, E. A. (1990). *North America workshop on monitoring for ecological assessment of terrestrial and aquatic ecosystems*. *General Technical Report RM, 284*.

Capuzzo, I. M. (1988). Biological effects of petroleum hydrocarbons on marine organisms: Integration of experimental results and predictions of impacts. *Marine Environmental Research, 17*, 272-276.

Clark Jr., R. C. & Brown, N. W. (1997). Petroleum properties and analysis in biotic and abiotic systems: An effect of petroleum on Arctic and sub-arctic marine environment organisms.

Clark, R. B. (1992). *Marine pollution*. Oxford University Press.

Davidson, D. & Deere, D. (2004). Risk assessment in water supply. *National Water Surveillance Conference, Dhaka, 4-6 July*.

Department of Petroleum Resources (DPR). (2002). *Environmental guidelines and standards for the petroleum industry in Nigeria (EGASPIN)*.

Egborge, A. B. M. (1991). Industrialization and heavy metals pollution in Warri River. *32th Inaugural Lecture, University of Benin, Benin City*.

Ekpo, B. O., Oyo-Ita, O. E., Oros, D. R. & Simoneit, B. R. T. (2012). Distribution and sources of polycyclic aromatic hydrocarbons in surface sediments from Cross River Estuary, S. E. Niger Delta. *Environmental Monitoring and Assessment, 184*(2), 1037-1047.

Ezekwe, I. C., Eludoyin, O. S. & Adigwu, O. (2015). Land use dynamics and mangrove forest decline in the Soku oil and gas fields, Niger Delta region of Nigeria. *Journal of Geographic Thought & Environmental Studies, 13*(1), 1-12. http://www.academix.ng/journals/profile.html?idd=3300010155

Ezekwe, I. C. & Utong, I. C. (2017). Hydrocarbon pollution and potential ecological risk of heavy metals in the sediments of the Oturuba Creek, Niger Delta, Nigeria. *Journal of Environmental Geography, 10*(1–2), 1–10. https://www.degruyter.com/downloadpdf/j/jengeo.2017.10.../jengeo-2017-0001.xml

Ezekwe, I. C. & Utong, I. C. (2015). Ecological risk levels from hydrocarbon and metal concentrations in the sediments of an oil-polluted coastal river in Andoni, Eastern Niger Delta of Nigeria. *Ponencia presentada en la International Conference of Water Resources and Environment, 25-28 de julio, Beijing, China.*

Federal Ministry of Environment Abuja, Nigerian Conservation Foundation Lagos, WWF UK y CEESP-IUCN Commission on Environmental, Economic and Social Policy. (2006, 31 de mayo). *Niger Delta resource damage assessment and restoration project*.

Field, L., MacDonald, D. D., Norton, S. B., Ingersoll, C. G., Severn, C. G., Smorong, D. & LindsKoog, R. (2002). Predicting amphipod toxicity from sediments using logistic regression models. *Environmental Toxicology and Chemistry, 9*, 1993-2005.

Gaiero, D. M., Ross, G. R., Depetris, P. J. & Kempe, S. (1997). Spatial and temporal variability of total non-residual heavy metals content in stream sediments from the Suquía River system, Córdoba, Argentina. *Water, Air, and Soil Pollution, 93*, 303-319.

Gao, X. & Chen, C. T. A. (2012). Heavy metal pollution status in surface sediments of the coastal Bohai Bay. *Water Resources, 46*, 1901-1911.

Ghaleno, O. R., Sayadi, M. A. & Rezaei, M. R. (2015). Potential ecological risk assessment of heavy metals in sediments of water reservoir: Case study: ChahNimeh of Sistan. *Department of Environmental Science, University of Birjand, Iran*.

Gwack, J., Lee, J. H., Kang, Y. A., Cheng, K. J., Lee, M. S. & Hong, J. Y. (2012). Acute health effect among military personnel participating in the cleanup of the Hebei Spirit oil spill, 2007, in TapanComty, Korea. *Oson Public Health and Research Prospect, 3*(4), 206-212.

Hakanson, L. (1980). An ecological risk index for aquatic pollution control: A sedimentological approach. *Water Research, 14*, 975-1001.

Hart, B. T. (2004). Environmental risks associated with new irrigation schemes in northern Australia. *Ecological Management and Restoration, 5*, 107-111.

Hayes, E. H. & Landis, W. A. (2004). Regional ecological risk assessment of a near shore environment: Cherry Point, WA. *Human and Ecological Risk Assessment, 10*, 299-325.

Howard, I. C., Gabriel, U. U. & Horsfall, M. (2009). Evaluation of total hydrocarbon levels in some aquatic media in an oil-polluted mangrove wetland in the Niger Delta. *Applied Ecology and Environmental Research, 7*(2), 111-120.

Huang, X. P., Huang, L. M. & Yue, W. Z. (2003). The characteristics of nutrients and eutrophication in the Pearl River Estuary, South China. *Marine Pollution Bulletin, 47*, 30-36.

Ikwobodo, O. C. (2014). *Impact of oil pollution on Bomu River/Estuary in Gokana Local Government Area of Rivers State* (Tesis de maestría inédita). Department of Geography and Environmental Management, University of Port Harcourt, Nigeria.

International Maritime Organization (IMO). (2000). *Guidance on assessment of sediment quality. Global investigation pollution in the marine environment (GIPME)* (Pub. No. 439/00). IOC-UNEP-IMO.

International Union for the Conservation of Nature and Natural Resources. Niger Delta Panel (IUCN-NDP). (2013). *Soku biophysical report: Sustainable remediation and rehabilitation of biodiversity and habitat of oil spill sites in the Niger Delta*. IUCN.

IUCN/CEESP. (2006). *Niger Delta natural resources damage assessment and restoration project: Phase 1 scoping report*. IUCN Commission on Environment, Economic and Social Policy.

James, P. E. (1972). *All worlds: A history of geographical ideas*. The Odyssey Press.

Jing, L. (2014). Risk assessment of heavy metals in surface sediments from the Yanghe River, China. *Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, Beijing, China*.

Levinson, A. & Scott, M. (2008). Unmasking the pollution haven effect. *International Economic Review, 49*(1), 223-254.

Li, X., Liu, L. & He, X. (2012). Integrated assessment of heavy metal contamination in sediments from a coastal industrial basin, NE China. *PLOS One, 7*(6), e39690.

Long, E. R. & Morgan, L. G. (1990). The potential for biological effects of sediment-sorbed contaminants tested in the National Status and Trends Program. *Technical Memorandum NOS OMA 52*. National Oceanic and Atmospheric Agency (NOAA).

Luoma, S. N. (1997). Processes affecting metal concentrations in estuarine and coastal marine sediments. En R. W. Furness y P. S. Rainbow (Eds.), *Heavy metals in the marine environment* (pp. 256). CRC Press.

MacDonald, D. D., Dipinto, L. M., Field, L. J., Ingersoll, C. G., Long, E. R. & Swartz, R. C. (2000). Development and evaluation of consensus-based sediment effect concentrations for polychlorinated biphenyls (PCB). *Environmental Toxicology and Chemistry, 19*, 1403-1413.

Marcus, A. C. & Ekpete, O. A. (2014). Impact of discharged process wastewater from an oil refinery on the physicochemical quality of a receiving waterbody in Rivers State, Nigeria. *IOSR Journal of Applied Chemistry, 7*(12), 1-8.

Markou, D. A., Sylaios, G. K., Tsihrintzis, V. A., Gikas, G. D. & Haralambidou, K. (2007). Water quality of Vistonis Lagoon, Northern Greece: Seasonal variation and impact of bottom sediments. *Desalination, 210*(1), 83-97.

Mendelssohn, I. A., Andersen, G. A., Baltz, D. M., Caffey, R. H., Carman, A. R., Fleeger, J. W., Joye, S. B., Lin, Q., Maltby, E., Overturn, E. B. & Rozas, L. P. (2012). Oil impacts on coastal wetlands: Implications for the Mississippi River Delta ecosystem after the Deepwater Horizon oil spill. *Bioscience, 62*(6), 562-576. https://www.biosciencemag.org

Muller, G. (1969). Index of geo-accumulation in sediment of the Rhine River. *GeoJournal, 2*, 108-118.

Ndi, E. N. (2010, 4 de enero). *Vanguard News*. http://www.vanguardngr.com/2010/10/45980

Ndubuisi, A. L. & Asia, I. O. (2007). Environmental pollution in oil-producing areas of the Niger Delta Basin, Nigeria: Empirical assessment of trends and people's perception. *Environmental Research Journal, 1*(1-4), 18-26.

National Research Council (NRC). (2003). *Oil in the sea III: Inputs, fates and effects*. National Academic Press.

Nie, M., Xian, N., Fu, X., Chen, X. & Li, B. (2010). The interactive effect of petroleum hydrocarbon spillage and plant rhizosphere on concentrations and distribution of heavy metals in sediments in the Yellow River Delta, China. *Journal of Hazardous Materials, 174*(1-3), 156-161.

Nwaogbidi, I. C. (2015). *Assessing air quality impact from gas flaring in the Idu-Obagi oil and gas fields of South-South Nigeria* (Tesis de maestría). School of Postgraduate Studies, University of Port Harcourt, Nigeria.

Nwilo, P. C. & Badejo, O. T. (2007). Comps, impacts and management of oil spill pollution along the Nigerian coastal areas. http://fig.net/pub/figpub/pub36/chapters/chapter8.pdf

Odokuma, L. O. & Okpokwasili, G. C. (2004). Seasonal ecology of hydrocarbon-utilizing microbes in the surface waters of a river. *Environmental Monitoring and Assessment, 27*(3), 175-191.

Ohio Environmental Protection Agency. (2010). *Guidance on evaluating sediment contaminant results*. Division of Surface Water, Standards and Technical Support Section. http://www.epa.ohio.gov/portals/35/guidance/sediment_evaluation_jan10.pdf

Okereke, J. J., Obiekezie, S. O. & Obasi, K. O. (2007). Microbial flora of oil-spilled sites in Egbema, Imo State, Nigeria. *African Biotechnology, 6*(8), 991-993.

Omo-Irabor, O. O., Olobaniyi, S. B., Akunma, J., Venus, V., Maina, J. M. & Paradzayi, C. (2011). Mangrove vulnerability modelling in parts of western Niger Delta, Nigeria using satellite images, GIS techniques and spatial multi-criteria analysis (SMCA). *Environmental Monitoring and Assessment, 178*(1-4), 39-51.

Onuoha, F. C. (2008). Oil pipeline sabotage in Nigeria: Dimensions, actions and implications for national security. *African Security Review, 17*(3).

Pacz, O. F., Osuna, I. J. I., Izaquirre, G. G. & Zazueta, P. H. M. (1993). Heavy metals in oysters from a subtropical coastal lagoon associated with an agricultural drainage basin. *Bulletin of Environmental Contamination and Toxicology, 50*, 696-702.

Pazi, I. (2011). Assessment of heavy metal contamination in Candarli Gulf sediment, Eastern Aegean Sea. *Environmental Monitoring and Assessment, 174*, 199-208.

Pickett, S. T. A., Burch, W. R. Jr., Dalton, S. E., Foresman, T. W., Grove, J. M. & Rowntree, R. (1997). A conceptual framework for the study of human ecosystems. *Urban Ecosystems, 1*, 185-199.

Pluske, W., Murphy, D. & Sheppard, J. (2016). *Total organic carbon: Soil quality factsheets.* http://www.soilquality.org.au/factsheets/organic-carbon

Rapoport, A. (1968). General system theory. *International Encyclopedia of the Social Sciences, 15*, 452-458.

Rhoads, B. L. & Cahill, R. A. (1999). Geomorphological assessment of sediment contamination in an urban stream system. *Applied Geochemistry, 14*(4), 459-483.

Rivers State Ministry of Environment. (2009). *Oil spill inspection report in Rivers State, Nigeria*.

Rodrigues, M. L. K. & Formos, M. L. L. (2006). Geochemical distribution of selected heavy metals in stream sediments affected by tannery activities. *Water, Air, and Soil Pollution, 169*, 167-184.

Shell Petroleum Development Company Ltd. (SPDC). (2014). *Incidents of crude oil spillages above 50 barrels from 1976 up to 1999*. SPDC Ltd.

Singh, M., Müller, G. & Singh, I. B. (2003). Heavy metals in sediments of the Ganges River, India. *Journal of Geochemical Exploration, 80*, 1-17.

Singh, V. K., Singh, K. P. & Mohan, D. (2005). Status of heavy metals in water and bed sediments of River Gomti – A tributary of the Ganga River, India. *Environmental Monitoring and Assessment, 105*, 43-67.

Society of Environmental Toxicology and Chemistry (SETAC). (1997). *Technical issue paper: Ecological risk assessment*. SETAC.

Suter, G. W. II. (1993). *Ecological risk assessment*. Lewis Publishers.

The New South Wales Office of Environment and Heritage. (2015). *Soil survey standard test method*. http://www.environment.nsw.gov.au/resources/soils/testmethods/ocpdf

Thornton, I., Li, X. D., Wai, O. W. H., Li, Y. S., Coles, B. J. & Ramsey, M. H. (2000). Heavy metal distribution in sediment profiles of the Pearl River Estuary, South China. *Applied Geochemistry, 15*, 567-581.

Tomlinson, D. L., Wilson, J. G., Harris, C. R. & Jeffery, D. W. (1980). Problems in the assessment of heavy metal levels in estuaries and the formation of a pollution index. *Helgoländer Wissenschaftliche Meeresuntersuchungen, 33*, 566-572.

Tiessen, H. & Moir, J. O. (1993). Total and organic carbon. En M. E. Carter (Ed.), *Soil sampling and methods of analysis* (pp. 187-211). Lewis Publishers.

Twumasio, Y. & Merem, E. (2006). GIS and remote sensing application in the assessment of change within a coastal environment in the Niger Delta Region of Nigeria. *International Journal of Environmental Research and Public Health, 3*(1), 98-106.

Ukoli, M. K. (2005). Environmental factors in the management of the oil and gas industry in Nigeria. *Central Bank of Nigeria*. www.cenbank.org

United Nations Development Programme (UNDP). (2006). *History of environmental change in the Sistan Basin, based on satellite image analysis: 1976-2005*. UNEP Post-Conflict Branch.

United Nations Development Programme (UNDP). (2011). *Niger Delta human development report*. http://hdr.unde.org/en/reports/nationalreports/africa/nigeria/name,3368,en.html

United Nations Environment Programme (UNEP). (2011). *Environmental assessment of Ogoniland*. UNEP. www.unep.org/.../ogoniland.../UNEP_Ogoni.....

U.S. Environmental Protection Agency (USEPA). (1992). *Sediment classification methods compendium*. Sediment Oversight Technical Committee, Office of Water (WH-556). EPA 823-R-92-006.

U.S. Environmental Protection Agency (USEPA). (1996). *Proposed guidelines for ecological risk assessment. Federal Register, 61*, 47552-47631.

U.S. Environmental Protection Agency (USEPA). (1998). *Guidelines for ecological risk assessment*. EPA/630/R-95/002F.

U.S. Environmental Protection Agency (USEPA). (2003). *Procedures for the derivation of equilibrium partitioning sediment benchmarks (ESBs) for the protection of benthic organisms: PAH mixtures*. EPA600-R-02-013.

U.S. Environmental Protection Agency (USEPA). (2005). *Procedures for the derivation of equilibrium partitioning sediment benchmarks (ESBs) for the protection of benthic organisms: Metal mixtures (Cadmium, Copper, Lead, Nickel, Silver and Zinc)*. EPA600-R-02-011.

U.S. Environmental Protection Agency (USEPA). (2008). *Procedures for the derivation of equilibrium partitioning sediment benchmarks (ESBs) for the protection of benthic organisms*. EPA-60-R-02-016.

U.S. Environmental Protection Agency (USEPA). (2013). *Non-hazardous waste management hierarchy*. http://www.epa.gov/osw/nonhaz/municipal/hierarchy.htm

Verbruggen, E. M. J. (2004). *Environmental risk limits for mineral oil (total petroleum hydrocarbons)*. RIVM Report 601501021/2004.

Walkley, A. & Black, L. A. (1934). An examination of the Degtjareff method for determining organic carbon in soils: Effect of variations in digestion conditions and of inorganic soil constituents. *Soil Science, 63*, 251-263.

Xia, Z. et al. (2010). Health risk assessment on dietary exposure to polycyclic aromatic hydrocarbons (PAHs) in Taiyuan, China. *Science of the Total Environment, 408*, 5331-5337. https://doi.org/10.1016/j.scitotenv.2010.08.008