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HEAVY METALS POLLUTION AND OTHER PHYSICOCHEMICAL PARAMETERS IN THE CRUDE OIL-IMPACTED SANTA BARBARA RIVER AND ENVIRONS, BAYELSA STATE, NIGERIA

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ABSTRACT: *Higher levels of heavy metals in aquatic environments are most likely influenced by crude oil spills which may induce significant risk of heavy metal toxicity in aquatic species and humans. This research evaluated the levels of heavy metals and other physicochemical parameters in the crude oil-impacted Santa-Barbara River and environs of Bayelsa State, Nigeria. Heavy metals and other physicochemical parameters were examined using standard methods. Heavy metal pollution status was then deduced with standard pollution indicators. The water and fish samples collected from crude oil-impacted Santa Barbara River were heavily and moderately contaminated with iron, respectively (Igeo index = 4.29 and 2.87 for water and fish, respectively) and highly polluted with examined heavy metals (PLI = 4.29 and 1.13 for water and fish, respectively). The water samples from hand-dug wells were moderately contaminated with iron (Igeo index = 2.87) with overall low pollution by heavy metals (PLI = 0.46), while fish sold in neighboring communities was moderately contaminated with iron (Igeo index = 2.98) with overall moderate pollution by heavy metals (PLI = 0.86). However, potential ecological risks mediated by examining heavy metals in all water and fish samples were generally low (RI < 40). The total dissolved solids, biochemical oxygen demand, nitrate and phosphate concentrations in all water samples were within permissible limits of WHO and FEPA. The ecological risks associated with water and fish from all sampling locations were deduced as low, mainly because iron was the most abundant heavy metal contaminant with no significant toxic response.*

KEYWORDS: Heavy metals, Pollution load index (PLI), Potential ecological risk (RI), Toxicity.

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INTRODUCTION

Crude oil is a composite of hydrocarbon and non-hydrocarbon compounds (including heavy metals) near subsurface deposits worldwide [1]. Crude oil spills are the origins of heavy metal pollution of aquatic and terrestrial environments, particularly in oil-producing regions [2, 3]. Crude oil spills, which cause petroleum to be released into the natural environment, are often linked with activities, such as oil bunkering and sabotage, accidents, dearth of maintenance of engineering equipment, as well as crude oil extraction and refining, including shipping and storage of crude oil [2, 4, 5]. The Niger Delta region of Nigeria, the hub of crude oil activities in Nigeria, encounters a huge number of oil spill incidents [3]. The depth of crude oil exploration activities in this region manifests that Nigeria obtains over 80% of its national income from crude oil [4]. Due to the contamination of the Niger Delta region of Nigeria with considerable amounts of heavy metals as a result of crude oil spills, the inhabitants of this region may most likely be at risk of heavy metal toxicity, inclusive of aquatic species [6].

The presence of high concentrations of crude oil toxicants such as heavy metals in aquatic habitats could negatively affect the community of aquatic species by their propensity to harm their reproduction and survival as well as provoke migration of aquatic species such as fish [7, 8]. The possibility of the heavy metal toxicants accumulating in fish also exposes human consumers to these heavy metals' toxic effects [9, 10, 11]. Exposure to heavy metals like arsenic, cadmium, mercury, nickel, chromium and lead is known to cause toxic cellular effects such as a high risk of cardiovascular, neurological and dermatological reproductive diseases in humans [12].

Tchounwou *et al*. [13] reported that co-exposure to more than one heavy metal can give rise to effects that are more hazardous to human health than those brought about by exposure to individual heavy metals. The poor access to potable water by the majority of the inhabitants in the Niger Delta region has made it impossible for them to avoid drinking or cooking with water from sources that are contaminated with these heavy metals, irrespective of their awareness of the associated risks.

The concentrations of different heavy metals in a handful of locations/communities in the Niger Delta region have been carried out. Oribhabor and Ogbeibu [14] reported that the concentrations of heavy metals in surface water from Buguma Creek were within permissible World Health Organisation limits [15]. Ubiogoro and Adeyemo [16] found that most heavy metals in water and fish samples collected from the Gbokodo River in Warri, Urie River in Igbide Isoko, River Ethiope in Sapele, Aragba River in Abraka, Uzere creek and Asaba-Ase creek were within the WHO limits, except for nickel and iron which were higher than the recommended limits in fish. Owamah [17] reported that the concentrations of lead, nickel, copper, chromium, iron, copper, cadmium and mercury in surface water from the Ijana River, Warri, were higher than the WHO limits. Ejike *et al*. [18] also found that lead, arsenic, and cadmium were in concentrations that were above the WHO's recommended limits for drinking water. Symptoms reported to be prevalent among the local inhabitants include dizziness, vomiting, abdominal pain, nausea, vomiting and headache [19]. The present research sought to evaluate the levels of heavy metals and other physicochemical parameters in the crude oil-impacted Santa-Barbara River and Environs, Bayelsa State, Nigeria.

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MATERIALS AND METHODS

Description of the Study Area

The geographical coordinates of Santa Barbara River are Latitude 4.3358,4^o 20. 89" North and Longitude 6.6022, 6^o 36. 81" East. It is located in the Nembe Local Government Area of Bayelsa State, Nigeria, south of the Brass Creek and east of the Odiame Creek. Over two million barrels of oil and gas were emptied into the Santa Barbara River from a blowout by Nigerian National Petroleum Corporation and AITEO Exploration and Production Company Limited OML-29-WELL-1, which occurred on the 5^{th} of November 2021. The spills were later disseminated into creeks and waterways in Kula and neighboring communities, such as Angbakiri, Kalawo kiri, New Camp, Aberebiya, Arapakama, Inemaboko, Robert Kiri, Belama and Ofoinama. The spills were stopped on 8 December 2021. The Santa Barbara River runs into the Atlantic Ocean, and several communities surrounding the Santa Barbara River are rural. The map of the study area is shown in Figure 1.

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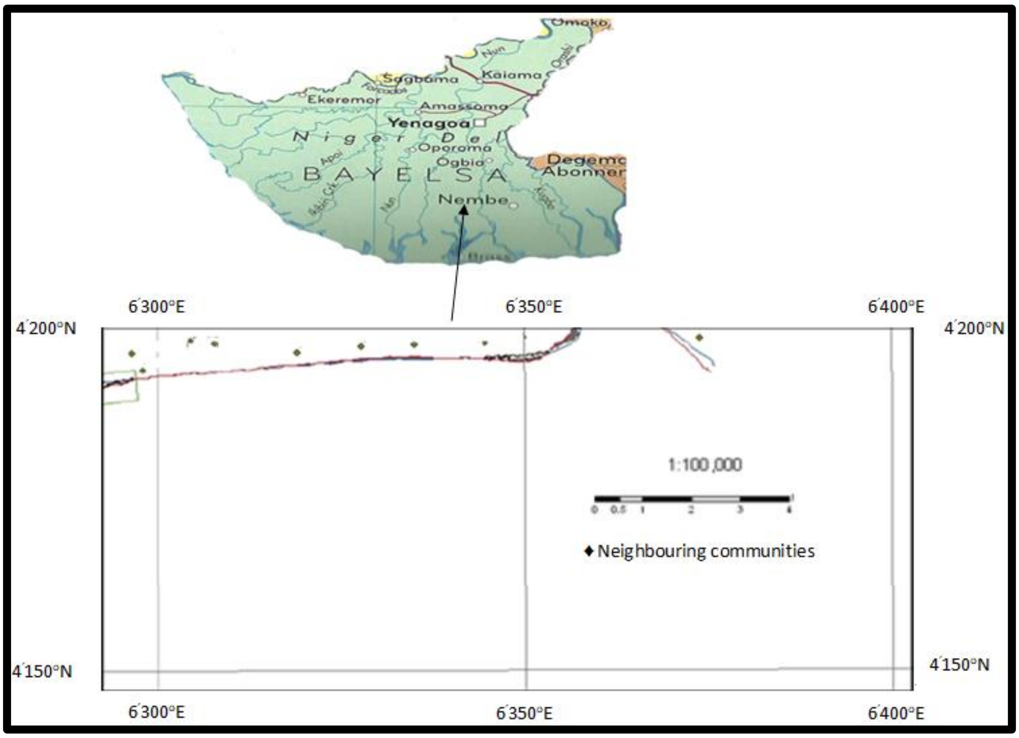

Figure 1: Map showing Bayelsa State and a description of the Santa Barbara River and its coastline situated in Nembe

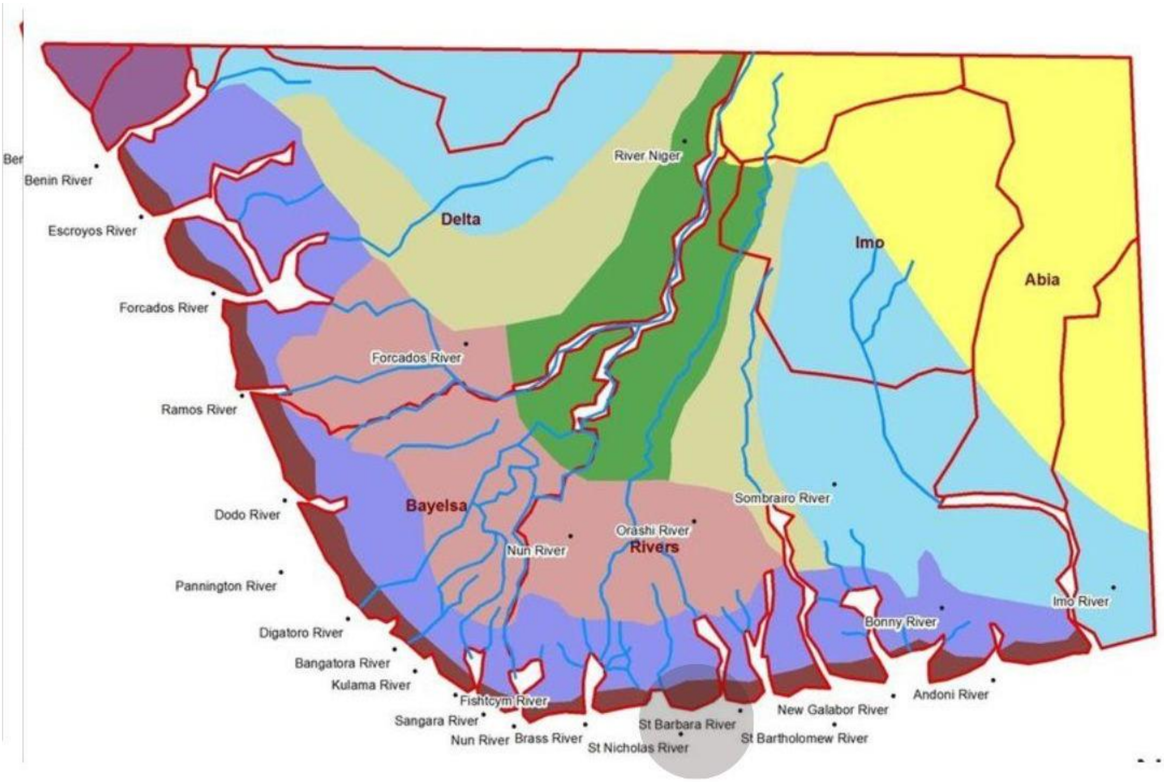

Figure 2: Map showing Bayelsa State and a description of the Santa Barbara River and its coastline situated in Nembe

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Study Design

Santa Barbara River was visited four times between May and August 2022 to collect samples. On each visit, crude oil-impacted water samples and fish samples were randomly collected in triplicate. The water samples were collected by scooping them into calibrated sterile containers to a depth of 15 cm. In contrast, the fish samples were collected with a fishing net and transferred into reclined polyethene bags. Sampling was at five different points along the downstream station of the Santa Barbara River over a distance of 500 to 800 meters away from the drilling facilities of Santa Barbara Flow Station (OML-29). Overall, 60 crude oil-impacted water samples and fish samples were collected from 20 sampling points along the Santa Barbara River. A total of 12 control water and fish samples were collected from sampling points along the upstream station of the Santa Barbara River over 1000 meters away from the drilling facilities where crude oil spillage has minimal influence. Other collected samples included water samples from hand-dug wells and fish samples sold in communities surrounding the Santa Barbara River. These samples were collected in triplicates from five different sampling locations on each visit. All the pieces were transported to the laboratory in a thermos flask with ice for physicochemical analyses, which were conducted within 12 hours of sample collection. Physicochemical analyses were carried out by compositing triplicate samples from each sampling point/location obtained at each visit of the study sites and examining them as a single sample.

Each sample was assigned to four independent treatment groups using the iterative Wei's Urn randomisation model [20]. The treatments that were performed included measurements of physical and inorganic parameters such as temperature, pH, conductivity (EC), total dissolved solids (TDS), total suspended solids (TSS), turbidity, dissolved oxygen (DO), Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD) and salinity, as well as the measurement of heavy metals such as zinc, iron, nickel, copper, chromium, lead and cadmium that were used to calculate the degree of contamination and the potential ecological risk associated with heavy metals in the Santa Barbara River and environs.

Preparation of Samples

All the samples were acidified using hydrochloric acid to reduce the pH to less than 2 to prevent the precipitation of metals. The scales of the fish samples were removed, followed by washing with distilled water, after which the muscle portion of the fish was excised and oven-dried at 80^{o}C to a constant weight. The dried fish muscle was then macerated and sieved through a 1 mm mesh sieve to obtain a homogenized powdered fish sample from which aliquots were used for physicochemical analysis.

Physicochemical Analysis

The measurements of physicochemical parameters, such as temperature, pH, EC, TDS, TSS, turbidity, DO, BOD, COD, salinity, phosphates and nitrates in the samples were carried out using the standard methods prescribed by the American Public Health Association [21].

Heavy Metal Analysis

A flame atomic absorption spectrometer (FAAS) was used for the analysis of the heavy metal contents in the samples [21]. Calibration standards were prepared from AAS-grade reagents for all the metals of interest

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Calculation of Heavy Metal Pollution Status

Calculation of Contamination Factor

The contamination factor (Cf) evaluates the impact of a single heavy metal contamination in the crude oil-impacted water and its control from the Santa Barbara River, as well as water samples from hand-dug wells in communities surrounding the Santa Barbara River and fish samples from the crude oil-impacted Santa Barbara River and neighboring communities. Cf is defined as the concentration of an individual heavy metal to its background concentration (Håkanson, 1980) as expressed in Equation 1.

$$\text{contamination factor} = \frac{Concentration\ of\ a\ pollutant}{Background\ concentration\ of\ the\ pollutant} \qquad \text{(Eq. 1)}$$

Background concentrations (FEPA standard limits) for heavy metal pollutants are: Cadmium = 0.01 mg/l, Nickel = 1 mg/l; Lead = 0.05 mg/l; Iron = 0.05 mg/l; Copper = 5 mg/l; Zinc = 1 mg/l; Chromium = 0.2 mg/l. For the description of contamination factor by heavy metals, the following terminologies were used: $C_f < 1$ represents low contamination with the heavy metal; $1 \leq C_f \leq 3$ represents moderate contamination with the heavy metal; $3 \leq C_f \leq 6$ represents considerable contamination with the heavy metal; and $C_f > 6$ represents high contamination with the heavy metal [22].

Calculation of Pollution Load Index

Tomlinson's pollution load index (PLI) measured the combined contamination status of heavy metal pollutants in the samples [23]. It is mathematically expressed as the n^{th} root of the product of the *n* contamination factors as follows:

$$\text{PLI} = \sqrt[n]{Cf1 \times Cf2 \times Cf3 \times Cf4 \times Cf5 \ldots\ldots \times Cfn} \qquad \text{(Eq. 2)}$$

Cf is the contamination factor, and n is the number of heavy metals analyzed. PLI of less than 0.5 represents low pollution; when it is greater than 0.5, less than 1 represents moderate pollution. PLI of greater than 1 represents high pollution with heavy metals.

Calculation of Geoaccumulation Index

The geoaccumulation index (*Igeo*) measured the degree of contamination of heavy metal pollutants [24, 25]. The *Igeo* was calculated as follows:

$$Igeo = \log_2 \left(\frac{Cn}{1.5Bn}\right) \qquad \text{(Eq. 3)}$$

Cn is the concentration of nth heavy metal. 1.5 is a correction factor adopted to address possible variations in the background concentration of heavy metal attributed to lithogenic and anthropogenic effects. *Bn* is the geochemical background concentration of the heavy metal.

For the description of *Igeo*, the following terminologies were used: $Igeo \leq 0$ (practically uncontaminated); $1 < Igeo \leq 2$ (uncontaminated to moderately contaminated); $2 < Igeo \leq 3$ (moderately contaminated); $3 < Igeo \leq 4$ (heavily contaminated); $4 < Igeo \leq 5$ (heavily to extremely contaminated); $Igeo > 5$ (extremely contaminated).

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Calculation of Ecological Risk Factor

The ecological risk factor (Er) quantitatively expressed the potential ecological risk of heavy metal in the samples. It is expressed as follows:

$$Er = Tr \times Cf \qquad \text{(Eq. 4)}$$

Cf is the contamination factor. Tr is the toxic-response factor for the heavy metal. Values of the toxic-response factors for the heavy metals [26, 27] are: Lead =5; Cadmium = 30; Chromium = 2; Copper = 5; Mercury = 40; Nickel = 5; Zinc = 1.

Calculation of Potential Ecological Risk Index

The potential ecological risk index (*RI*) is the sum of a sample's risk factors. The ecological risk factor was calculated as follows:

$$RI = \sum_{n=1}^{\infty} Er \qquad (Eq. 3.5)$$

Where Er is the single index of ecological risk factor; ∞ *is the count of heavy metals.* The terminologies used for evaluating the potential ecological risk index of heavy metal pollutants were as follows [22]: *RI* < 40 (low potential ecological risk); 40 ≤ *RI* ≤ 80 (moderate potential ecological risk); 80 ≤ *RI* ≤ 160 (considerable potential ecological risk); 160 ≤ Er ≤ 320 (high potential environmental risk); *RI* > 320 (very high ecological risk).

Statistical Analysis

Descriptive statistics of the physical, inorganic and organic parameters were done with NCSS ver. 12 data analysis software. Shapiro–Wilk normality test, Levene test of homogeneity, parametric Student’s t-test and non-parametric Mann Whitney U (Wilcoxon rank-sum) test were also performed with NCSS ver. 12 data analysis software.

RESULTS

Heavy Metal Parameters in the Water Samples

The heavy metal constituents of the crude oil-impacted water and its control from the Santa Barbara River, as well as water samples from hand-dug wells in communities surrounding the Santa Barbara River, are presented in Table 4.1. Of the examined heavy metals, cadmium and nickel were not detected in all the water samples examined. Iron was the most abundant heavy metal detected in all water samples examined, with mean concentrations estimated at 1.47 ± 0.14 mg/l, 0.74 ± 0.15 mg/l and 0.55 ± 0.04 mg/l in crude oil-impacted water, control water and hand-dug well water samples, respectively. The non-parametric Mann-Whitney U (Wilcoxon rank-sum) test also revealed that concentrations of iron, chromium, lead and copper in the crude oil-impacted Santa Barbara River were significantly higher ($p < 0.05$) than those reported in the hand-dug wells. The student’s t-test indicated that concentrations of zinc in the crude oil-impacted River were not significantly different ($p > 0.05$) from those reported in the hand-dug wells. The decreasing order of heavy metals contamination of water from the crude

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oil-impacted Santa Barbara River and hand-dug wells was as follows: chromium>iron>copper>lead>zinc>cadmium/nickel for the crude oil-impacted river and iron>copper>chromium>zinc>lead>cadmium/nickel for the hand-dug wells.

Other Physicochemical Parameters in the Water Samples

Some physicochemical constituents of the crude oil-impacted water and its control from the Santa Barbara River, as well as water samples from hand-dug wells in communities surrounding the Santa Barbara River, are presented in Table 2. The pH of the crude oil-impacted water ranged from 5.50 to 6.64, with mean pH of 6.02 ± 0.09; while those of the control and hand-dug well ranged from 6.11 to 7.33 and from 5.20 to 6.31, respectively.

Table 1: Heavy metals examined in the water samples

Parameters	Samples examined			Maximum permissible limits	
	Crude oil-impacted water from Santa Barbara River H = 20	Control water from Santa Barbara River H = 4	Water from hand-dug well in communities surrounding the Santa Barbara River H = 20	FEPA 1991	WHO 2011
Iron (mg/l)	1.47 ± 0.14	0.74 ± 0.15	0.55 ± 0.04	0.05	0.03
Zinc (mg/l)	0.06 ± 0.006	0.69 ± 0.06	0.10 ± 0.007	1.00	5.00
Chromium (mg/l)	2.45 ± 0.15	0.24 ± 0.007	0.12 ± 0.007	0.05	0.20
Lead (mg/l)	0.10 ± 0.003	0.024 ± 0.003	0.02 ± 0.002	0.05	0.01
Copper (mg/l)	0.37 ± 0.05	0.23 ± 0.006	0.30 ± 0.01	2.00	5.00
Cadmium (mg/l)	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	5.00	1.00
Nickel (mg/l)	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	1.00	0.10

H: total number of composited samples examined. Mean values are presented as mean ± standard error of the mean. FEPA: Federal Environmental Protection Agency, Nigeria. WHO: World Health Organization

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Table 2: Physicochemical parameters examined in the water samples

Parameters	Samples examined			Permissible limits	
	Crude oil-impacted water from Santa Barbara River H = 20	Control water from Santa Barbara River H = 4	Water from hand-dug well in communities surrounding the Santa Barbara River H = 20	FEPA (1991)	WHO (2011)
Temperature (ºC)	27.79 ± 0.18	27.71 ± 0.24	28.02 ± 0.10	< 40.00	< 40.00
Turbidity (NTU)	21.02 ± 0.90	14.81 ± 0.63	8.66 ± 0.17	10.00	10.00
Electrical conductivity (µS/cm)	500.92 ± 17.14	352.74 ± 4.77	290.15 ± 3.04	1500.00	300.00
pH	6.02 ± 0.09	6.34 ± 0.09	5.81 ± 0.07	6.50 – 9.50	6.50 – 9.50
Dissolved oxygen (mg/l)	4.74 ± 0.20	5.46 ± 0.15	5.55 ± 0.09	> 5.00	> 5.00
Biochemical Oxygen Demand (mg/l)	2.75 ± 0.16	3.42 ± 0.20	7.36 ± 0.20	< 10.00	< 10.00
Chemical Oxygen Demand (mg/l)	11.73 ± 0.33	10.20 ± 0.27	9.38 ± 0.24	80.00	20.00
Total Dissolved Solids (mg/ml)	296.96 ± 5.02	156.11 ± 9.06	263.25 ± 4.13	2000.00	500.00
Total Suspended Solids (mg/l)	65.37 ± 3.21	118.58 ± 1.44	18.76 ± 0.54	30.00	30.00
Salinity (mg/l)	20.29 ± 0.74	18.64 ± 0.41	10.60 ± 0.56	2000.00	600.00
Phosphate (mg/l)	0.04 ± 0.002	0.11 ± 0.01	0.16 ± 0.004	5.00	5.00
Nitrate (mg/l)	0.02 ± 0.003	0.03 ± 0.003	0.02 ± 0.002	10.00	10.00

H: total number of composited samples examined. Mean values are presented as mean ± standard error of the mean. FEPA: Federal Environmental Protection Agency, Nigeria. WHO: World Health Organization

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The mean pH of the control water and hand-dug well were 6.34 ± 0.09 and 5.81 ± 0.07, respectively. Ninety per cent (90%) of the crude oil-impacted water samples had pH that was below the WHO and FEPA permissible limits (6.50 – 9.50) required in aquatic systems for the survival of aquatic life, while 80% of the control water samples had pH that was below the WHO and FEPA permissible limits (6.50 – 9.50) required in aquatic systems for the survival of aquatic life. All the water samples (100%) collected from the hand-dug wells had pHs which were below the WHO and FEPA permissible limits (6.50 – 9.50) for portable drinking water.

DO in the crude oil-impacted water samples ranged from 3.55 mg/l to 6.23 mg/l, with mean DO estimated at 4.74 ± 0.20, while in the control samples, DO values were between 5.10 mg/l and 6.32 mg/l, with mean value calculated at 5.55 ± 0.09 mg/l. The DO in the hand-dug well water samples ranged from 4.90 mg/l to 6.37 mg/l, with a mean value estimated at 5.46 ± 0.15 mg/l. As indicated by the Mann-Whitney U (Wilcoxon rank-sum) test, DO recorded in the crude oil-impacted Santa Barbara River were not significantly different ($p > 0.05$) from those recorded in the hand-dug wells.

Mean BOD and COD were respectively reported as 2.75 ± 0.16 mg/l and 11.73 ± 0.33 mg/l in the crude oil-impacted water samples and as 3.42 ± 0.20 mg/l and 10.20 ± 0.27 mg/l in the control samples; while they were estimated at 7.36 ± 0.20 mg/l and 9.38 ± 0.24 mg/l in the hand-dug well water samples.

The student's t-test indicated that datasets of TDS in the crude oil-impacted River were significantly higher relative to TDS datasets reported in the hand-dug wells. The non-parametric Mann-Whitney U (Wilcoxon rank-sum) test also revealed that TSS, turbidity and salinity of the crude oil-impacted Santa Barbara River were significantly higher ($p < 0.05$) than those reported in the hand-dug wells. The phosphate concentrations in the crude oil-impacted water significantly differed ($p < 0.05$) from those of the hand-dug wells. However, unlike the phosphate concentrations, nitrate concentrations in the crude oil-impacted Santa Barbara River were not significantly different ($p > 0.05$) from nitrate concentrations obtained from the hand-dug wells.

Heavy Metal Parameters in the Fish Samples

The heavy metal constituents of fish samples collected from the crude oil-impacted Santa Barbara River and communities surrounding the Santa Barbara River are presented in Table 3. Zinc was the most abundant heavy metal in all fish samples examined, with mean concentrations of 2.17 ± 0.45 mg/kg and 2.27 ± 0.57 mg/kg reported in fish samples from crude oil-impacted downstream Santa Barbara River and communities surrounding the Santa Barbara River, respectively. Amongst the array of heavy metals examined, cadmium, lead and nickel were not detected in all the fish samples examined. The student's t-test indicated that concentrations of iron, chromium, zinc and copper in fish from crude oil-impacted Santa Barbara River were not significantly higher ($p > 0.05$) than those reported in the fish sold in communities surrounding the Santa Barbara River. The decreasing order of heavy metals contamination of fish obtained from the crude oil-impacted Santa Barbara River and those sold in the neighboring communities followed a similar pattern: zinc>iron>copper>chromium>lead/cadmium/nickel.

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Heavy Metals Pollution Indicators in the Water Samples

Table 4 shows the pollution indicators used in evaluating the heavy metal pollution status of water samples collected from the Santa Barbara River and communities surrounding the Santa Barbara River. The *Igeo* index indicated that water from the crude oil-impacted Santa Barbara River was heavily contaminated with iron (*Igeo* index = 4.29), followed by moderate contamination with chromium (*Igeo* index = 3.03) and very low contamination with lead (*Igeo* index = 0.41).

Table 3: Heavy metals examined in the fish samples

Parameters	Samples examined		Maximum permissible limits	
	Fish from the crude oil-impacted Santa Barbara River H = 20	Fish sold in communities surrounding the Santa Barbara River H = 20	FEPA	WHO
Iron (mg/kg)	0.55 ± 0.05	0.59 ± 0.06	0.50	0.50
Zinc (mg/kg)	2.17 ± 0.45	2.27 ± 0.57	60.00	40.00
Chromium (mg/kg)	0.23 ± 0.02	0.10 ± 0.02	0.15	0.10
Lead (mg/kg)	0.00 ± 0.00	0.00 ± 0.00	2.00	2.00
Copper (mg/kg)	0.28 ± 0.05	0.20 ± 0.04	3.00	3.00
Cadmium (mg/kg)	0.00 ± 0.00	0.00 ± 0.00	0.50	0.50
Nickel (mg/kg)	0.00 ± 0.00	0.00 ± 0.00	0.60	0.50

H: total number of composited samples examined. Mean values are presented as mean ± standard error of the mean.

FEPA: Federal Environmental Protection Agency, Nigeria. WHO: World Health Organization

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Table 4: Heavy metals pollution indices for the different water samples

Samples examined	Pollution indicators	Heavy metals examined							
		Iron	Zinc	Chromium	Lead	Copper	Cadmium	Nickel	
Crude oil-polluted	Contamination factor (Cf)	29.40	0.06	12.25	2.00	0.07	0.00	0.00	
water downstream	Pollution load index (PLI)								1.25
Santa Barbara	Degree of contamination (*Igeo* index)	4.29	0.00	3.03	0.41	0.00	0.00	0.00	
River	Ecological risk factor (Er)	NA	0.06	24.50	10.00	0.35	0.00	0.00	
	Potential ecological risk index (RI)								34.91
Control water	Contamination factor (Cf)	14.80	0.69	1.20	0.48	0.05	0.00	0.00	
upstream	Pollution load index (PLI)								0.78
Santa Barbara	Degree of contamination (*Igeo* index)	3.30	0.00	0.00	0.00	0.00	0.00	0.00	
River	Ecological risk factor (Er)	NA	0.69	2.40	2.40	0.25	0.00	0.00	
	Potential ecological risk index (RI)								5.75
Water from hand-	Contamination factor (Cf)	11.00	0.10	0.60	0.40	0.06	0.00	0.00	
dug well in	Pollution load index (PLI)								0.46
Communities	Degree of contamination (*Igeo* index)	2.87	0.00	0.00	0.00	0.00	0.00	0.00	
surrounding the	Ecological risk factor (Er)	NA	0.10	1.20	2.00	0.30	0.00	0.00	
Santa Barbara	Potential ecological risk index (RI)								3.60
River									

NA: toxic-response factor not available

The crude oil-impacted water was not contaminated with zinc, copper, cadmium and nickel. The control water from the upstream Santa Barbara River and water from hand-dug wells in communities surrounding the Santa Barbara River were also heavily/moderately contaminated with iron (*Igeo* index = 3.30 and 2.87, respectively). Contamination of these samples with zinc, chromium, lead, copper, cadmium and nickel was insignificant. The crude oil-impacted Santa Barbara River was highly polluted with heavy metals, as indicated by a PLI 1.25, while low pollution with heavy metals was found in the hand-dug wells (PLI = 0.46). Chromium was the heavy metal that most significantly contributed to the ecological risk mediated by heavy metals in the crude oil-impacted Santa Barbara River, as indicated by an Er of 24.50. However, lead was found to be the heavy metal that most significantly contributed to ecological risk mediated by heavy metals in the hand-dug well (Er = 2.00). Based on all the heavy metals examined, the potential ecological risk mediated by these heavy metals in water from the crude oil-polluted Santa Barbara River was suspected to be low (RI < 40); likewise, in the water from the hand-dug wells with RI of 3.60.

Heavy Metals Pollution Indicators in the Fish Samples

The pollution indices used in assessing the heavy metal pollution status of fish samples collected from the Santa Barbara River and those sold in communities surrounding the Santa Barbara River are presented in Table 5. The *Igeo* index showed that fish samples collected from the crude oil-impacted Santa Barbara River and from those sold in communities surrounding the Santa Barbara River were moderately contaminated with iron (Igeo index = 2.87 and 2.98, respectively), followed by very low contamination with zinc (*Igeo* index = 0.54 and 0.60, respectively). The fish from crude oil-impacted Santa Barbara River was highly polluted with heavy metals (PLI > 1.00). In contrast, those sold in communities surrounding the Santa Barbara River were moderately polluted with heavy metals (PLI = 0.86).

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Table 5: Heavy metals pollution indices for the different fish samples

Samples examined	Pollution indicators	Heavy metals examined							
		Iron	Zinc	Chromium	Lead	Copper	Cadmium	Nickel	
Fish from crude oil-polluted water downstream Santa Barbara River	Contamination factor (Cf)	11.00	2.17	1.15	0.00	0.06	0.00	0.00	
	Pollution load index (PLI)								1.13
	Degree of contamination (*Igeo* index)	2.87	0.54	0.00	0.00	0.00	0.41	0.00	
	Ecological risk factor (Er)	NA	2.17	2.30	0.00	0.30	0.00	0.00	
	Potential ecological risk index (RI)								4.77
Fish sold in communities surrounding the Santa Barbara River	Contamination factor (Cf)	11.80	2.27	0.50	0.00	0.04	0.00	0.00	
	Pollution load index (PLI)								0.86
	Degree of contamination (*Igeo* index)	2.98	0.60	0.00	0.00	0.00	0.00	0.00	
	Ecological risk factor (Er)	NA	2.27	1.00	0.00	0.20	0.00	0.00	
	Potential ecological risk index (RI)								3.47

NA: toxic-response factor not available

Chromium was the heavy metal that most significantly contributed to the ecological risk mediated by heavy metals in the fish collected from crude oil-impacted Santa Barbara River (Er of chromium = 2.30) and also from those sold in communities surrounding the Santa Barbara River (Er of chromium = 1.00). Based on all the heavy metals examined, the potential ecological risk mediated by these heavy metals in fish from the crude oil-impacted Santa Barbara River and those sold in communities surrounding the Santa Barbara River were suspected to be low (RI < 40).

DISCUSSION

It is an acknowledged fact that environmental pollution issues associated with petroleum exploration and production exist in the Niger Delta area of Nigeria. The task over the quality of crude oil-polluted waters applies not just to the water itself, but also to the risk of diffusion of toxic substances into other ecosystems [28, 29, 30].

The presence of high concentrations of crude oil toxicants such as heavy metals in aquatic habitats could adversely affect the population of aquatic species by their propensity to harm their reproduction and survival, as well as provoke the migration of aquatic species such as fish [7]. The pH values reported in crude oil-impacted water samples from Santa-Barbara River in this research (mean value = 6.02 ± 0.09) agreed with pH values reported by Aghoghovwia and Ohimain [31] and Seiyaboh *et al.* [32] in water samples collected from Kolo and Sagbama creeks situated in the Niger Delta region of Nigeria. However, the pH values of crude oil-impacted water sampled from the Santa Barbara River were at variance with the findings of Vincent-Akpu *et al.* [33] and Iwegbue *et al.* [34], who reported pH values in the alkaline range in water samples collected from the Bodo and Bomadi creeks situated in the Niger Delta region of Nigeria. The pH values reported in water samples from the hand-dug wells (mean value = 5.81 ± 0.07) from communities surrounding the Santa Barbara River were by those reported in the study of Akhionbare *et al.* [35] who worked on water samples from hand-dug wells in Burutu Community, Delta State, Nigeria. The low pH observed in water from the hand-dug

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wells may be due to the migration of salt water from the creeks, which modifies the acid-base equilibrium of the neighboring water table.

The concentrations of TDS in water bodies are significantly influenced by the geological materials of the water [34]. The TDS reported in the crude oil-impacted water samples from Santa-Barbara River (mean value = 296.96 ± 5.02 mg/l) were found to be within the limits of ≤ 500 mg/l and ≤ 2000 mg/l recommended by the World Health Organization [15] and Federal Environmental Protection Agency of Nigeria [21], as well as below the limits of TDS (500 – 48000 mg/l) often measured in brackish water [36]. The TDS values reported in water samples collected from hand-dug wells (mean value = 263.25 ± 4.13 mg/l) in communities surrounding the Santa Barbara River were also within the WHO and FEPA limits. The TDS values of this research were similar to those reported in the study of Akhionbare et al. [35], who worked on water samples from hand-dug wells in Burutu Community, Delta State, Nigeria.

Perturbation of particulate organic matter sediments at the bottom of the river can increase the concentration of suspended solids in the river, thereby causing several complications for aquatic life forms [37, 38]. The TSS reported in the crude oil-impacted water from Santa Barbara River (mean value = 65.37 ± 3.21 mg/l), which was above the WHO and FEPA limits (≤ 30 mg/l), was similar to those reported by Iwegbue *et al.* [34] in water from Bomadi creek; but was at variance with the values of TSS reported in the study of Effendi *et al.* [39] who worked on oil-spilled water collected from the coastal area of Karawang, Indonesia. TSS concentrations in water samples collected from the hand-dug wells (mean value = 18.76 ± 0.54 mg/ml) in communities surrounding the Santa Barbara River were within the limits recommended by WHO and FEPA. The TSS values reported in the study of Akhionbare *et al.* [35], who worked on water samples from hand-dug wells in Burutu Community, Delta State, Nigeria, were lower than those reported in this research.

Pollution of river water by crude oil could curtail the aeration of the water and, hence, DO. DO level in the range of 4 mg/l to 5 mg/l is the acceptable level required to maintain a fish community in an aquatic environment, but at levels below three mg/l, fish mortality becomes pronounced [40]. DO levels reported in the crude oil-impacted water (mean value = 4.74 ± 0.20 mg/l) examined in this research were mainly in the range that could still maintain fish population in the Santa Barbara River. Similar acceptable DO levels have been reported in the studies of Wokoma and Njoku [41] who worked on water from the Lower Sombreiro River in Niger Delta, Nigeria; and of Iwegbue *et al.* [34] who analyzed water from Bomadi Creek; as well as the study of Effendi *et al.* [39] who worked on crude oil-spilled water collected from the coastal area of Karawang, Indonesia. DO concentrations in water samples collected from hand-dug wells (mean value = 5.55 ± 0.09 mg/l) examined in this research were higher than those reported in the study of Ejechi *et al.* (2007) who worked on water from hand-dug wells in the Niger Delta area.

BOD concentrations of less than 1 mg/l are categorized as unpolluted. In comparison, concentrations in the range of 2 mg/l to 9 mg/l are categorized as moderate pollution, and concentrations greater than ten mg/l are categorized as heavy pollution with organic matter [42]. The mean BOD concentration of 2.75 ± 0.16 mg/l reported in crude oil-impacted water from the Santa Barbara River indicated moderate pollution with organic matter.

Anthropogenic activities, such as run-off of domestic, industrial and agricultural wastes and the applications of detergents, are the significant factors that influence the presence of

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phosphates and nitrates in water bodies [43]. Extreme nitrate concentrations in water bodies can result in eutrophication, which hinders the growth and existence of aquatic organisms by reducing oxygen in water bodies. The nitrate and phosphate concentrations in the crude oil-impacted water samples (mean values of nitrate and phosphate = 0.02 ± 0.003 mg/l and 0.04 ± 0.002 mg/ml, respectively) were within the safe limits (≤ 10 mg/l and ≤ 5 mg/l for nitrates and phosphates, respectively) recommended by WHO and FEPA. The nitrate levels reported in the crude oil-impacted water in the present research were similar to those obtained in the study of Iwegbue *et al.* [34]. Still, they were at variance with nitrate values reported in the study of Wokoma and Njoku [41].

The concentrations of lead reported in the crude oil-impacted water samples (mean values = 0.10 ± 0.003 mg/l) of this research exceeded the WHO and FEPA permissible limits of 0.01 mg/l and 0.05 mg/l, respectively. The lead concentrations reported in this research were higher than those reported by Iwegbue *et al.* [34], Eremasi *et al.* [44] and Ighariemu *et al.* [45], who worked on water samples collected from Bomadi, Kolo and Ikoli creeks, respectively, but were similar to those reported in the study of Olu *et al.* [46] who analyzed surface water collected from Soku Oil Field Area in the Niger Delta region of Nigeria. The high concentrations of lead found in the crude oil-impacted water of this research are a pointer to a potential health risk, especially when used for domestic purposes. In this research, relatively lower concentrations of lead were found in water from the hand-dug wells (mean value = 0.02 ± 0.002 mg/l) compared to those of the crude oil-impacted water. Lead concentrations in water from the hand-dug wells were within the FEPA permissible limit of ≤ 0.05 mg/l but were higher than the WHO permissible limit of ≤ 0.01 mg/l. Unlike the findings of this research, lead was not detected in all the water samples from Burutu Community, Delta State, analyzed by Akhionbare *et al.* [35].

The copper concentrations in the crude oil-impacted water samples from the Santa Barbara River (mean value = 0.37 ± 0.05 mg/l) were within the regulatory limits set by WHO (≤ 2 mg/l) and FEPA (≤ 5 mg/l). The copper levels reported for the crude oil-impacted water in this research were higher than those reported by Eramasi *et al.* [44] who worked on surface water from Kolo Creek, Bayelsa State, as well as those reported by Iwegbue *et al.* [34], but were within the same range as those reported by Imasuen and Egai [49] in surface water from Aguobiri Community, Bayelsa State. Copper concentrations in water from the hand-dug wells (mean value = 0.30 ± 0.01 mg/l) of this research were also within WHO and FEPA permissible limits. These copper values were similar to those reported in the study of Akhionbare *et al.* [35].

Chromium levels in the crude oil-impacted water (2.45 ± 0.15 mg/l) reported in this research were higher than WHO and FEPA permissible limits of ≤ 0.05 mg/l and ≤ 0.2 mg/l, respectively. The crude oil-impacted water chromium levels reported in this research were higher than those reported in the study of Edori and Iyama [47], who worked on water from Edagberi Creek, Rivers State, Nigeria. The high concentrations of chromium observed in the crude oil-impacted Santa Barbara River can lead to divergent hematological problems in fish; though may not cause fish mortality in most cases [47]. Unlike the crude oil-impacted water, chromium levels in the water from the hand-dug wells (mean value = 0.12 ± 0.007 mg/l) were within the FEPA permissible limit, though higher than the WHO permissible limit.

The crude oil-impacted water examined in this research had zinc levels (mean value = 0.06 ± 0.006 mg/l) within the permissible limits of 5 mg/l and one mg/l recommended by WHO and

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FEPA, respectively. These zinc levels were similar to those reported in the study of Edori and Iyama [47], as well as those of Odoemelam *et al.* [48], who worked on water collected from the Orashi River, Rivers State. The zinc concentrations recorded in the hand-dug well water (mean value = 0.10 ± 0.00 mg/l) analyzed in this research were also within the regulatory limits recommended by WHO and FEPA. The zinc values were lower than those reported in the study of Akhionbare *et al.* [35].

The iron contents of the crude oil-impacted water (mean value = 1.47 ± 0.14 mg/l) analyzed in this research exceeded the permissible limits of WHO (≤ 0.03 mg/l) and FEPA (≤ 0.05 mg/l). These iron concentrations were higher than those reported in the studies of Edori and Iyama [47] and Iwegbue *et al.* [34], as well as those of Asonye *et al.* [50] who analyzed water from rivers, streams and waterways in Southern Nigeria, and those of Haxhibeqiri *et al.* [51] who worked on water from Drini Bardhe River, Kosovo. Iron contents in water from the hand-dug wells (mean value = 0.55 ± 0.04 mg/l) examined in this research were also higher than the limits set by WHO and FEPA. The concentrations of iron from hand-dug well water analyzed in this research were in accordance with those reported in the study of Akhionbare *et al.* [35]. The high level of iron in the hand-dug well water may most likely impact the taste of the water collected from the hand-dug wells examined in this research.

The zinc contents in fish collected from the crude oil-impacted Santa Barbara River (mean value = 2.17 ± 0.45 mg/l) were within the WHO and FEPA limits of ≤ 40 mg/kg and ≤ 60 mg/kg, respectively. These zinc concentrations reported in this research were higher than those reported in the study of Ifemeje and Destiny [51], who analyzed fish collected from crude oil-impacted Ekpan and Ogunu Rivers in Delta State, Nigeria; but was lower than those reported in the study of Akintujoye *et al.* [52] who worked on fish collected from the Ubeji River in Delta State, Nigeria.

Iron and copper concentrations in the fish collected from crude oil-impacted water (mean values = 0.55 ± 0.05 mg/l and 0.28 ± 0.05 mg/l for iron and copper, respectively) were also within the WHO and FEPA limits (≤ 0.5 mg/kg and ≤ 3 mg/kg for iron and copper, respectively). However, chromium was found to exceed the WHO permissible limit of 0.1 mg/kg and FEPA permissible limit of 0.15 mg/kg in fish collected from crude oil-impacted water (mean value = 0.23 ± 0.02 mg/l). All the heavy metals examined in this research were found to be within WHO and FEPA limits in all fish samples sold in communities surrounding the Santa Barbara River.

Chromium was the heavy metal that most significantly contributed to ecological risk (Er = 24.50) mediated by heavy metals in the crude oil polluted Santa Barbara River. In another study by Chris and Anyanwu [52] who analyzed water samples from crude oil-impacted Isaka-Bundu Mangrove Swamp in Rivers State, Nigeria, copper was found to be the heavy metal significantly contributing to heavy metal-mediated ecological risk. The pollution load index of the crude oil-impacted Santa Barbara River (PLI = 1.25) was at variance with those recorded in water from the Isaka-Bunda Swamp, thus, suggesting high anthropogenic loading at the crude oil-impacted Santa Barbara River.

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CONCLUSION

This research revealed that water and fish from crude oil-impacted Santa Barbara River was highly polluted with heavy metals, unlike water from the hand-dug wells in neighboring communities and fish sold in the neighboring communities where low and moderate pollution with heavy metals were observed, respectively. In spite of the heavy metal pollution levels in the crude oil-impacted Santa Barbara River, the ecological risks associated with water and fish from the Santa Barbara River and other sampling locations were deduced as low, mainly because iron, with no significant toxic response, was the most abundant heavy metal contaminant.

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