Original Research

A Study of Microbiological Contamination and Metal Toxicity from Artisanal Crude Oil Refining on Ecosystem Health

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Abstract

This research aimed to examine the environmental consequences of crude petroleum refining processes. Water and air samples, taken from locations both near and far from artisanal oil refinery areas, were analyzed following approved procedures. The results obtained revealed that the operation of artisanal oil refineries had substantial environmental impacts. It was noted that water samples from high-incidence areas exhibited the highest levels of TPH (mean ~561 μg/L), potentially toxic metals, HUB (mean ~31.33 cfu/mL), and HUF (mean ~16.87 cfu/mL). However, water samples in the high-incidence area had the lowest electrical conductivity and dielectric constant values. Similarly, the highest levels of

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VOCs, SO₂, CH₄, NO₂, CO, and NH₃, along with the lowest O₃ values, were recorded in high-emission zones. In rainwater and surface water, potentially toxic metal concentrations followed this pattern: $Zn>Cu>Ni>Pb>Cd>As$ and $Zn>Cu>Ni>Pb>Cd>As>Hg$, respectively. The TCR values indicated that the metal concentrations were within the tolerable carcinogenic risk range, while the non-carcinogenic risks were within acceptable levels (HI<1). The findings of this study emphasized the importance of fostering a cleaner environment and identifying the basic pollution caused by human activities.

Introduction

Air quality is severely affected by anthropogenic actions, including urbanization, poor waste management, agricultural practices, industrial processes, vehicle emissions, and various domestic activities [1]. Emissions resulting from human activities are abundant in dioxins, methane, carbon monoxide, ammonia, and nitrous oxide [2, 3]. Furthermore, anthropogenic actions can elevate the levels of microorganisms, particulate matter (PM), and volatile organic compounds (VOCs) in ecosystems, which have numerous health risks [4-6]. Health issues linked to environmental pollution depend on the age and health status of the individual. Children and sick individuals are more susceptible to pollution-related diseases compared to healthy adults with stronger immune systems [7, 8]. Pollution-borne diseases (asthma, bronchiolitis, cardiovascular diseases, and neurological disorders) are a major cause of death globally, leading to approximately 7 million fatalities a year [3, 7, 9]. Contaminated atmospheric particles can have disastrous effects on all environmental components. It can dissolve in precipitation and be washed down to the earth, directly polluting soil and water bodies [10-12]. Contaminated deposition indirectly contaminates the vegetation and food chain/web, having a cascading impact on the entire ecosystem [13]. The human body absorbs contaminated substances through three primary pathways: oral ingestion, dermal, and inhalation, resulting in the absorption of these toxic substances into the human body [13-16]. Despite the huge economic benefits of crude oil, its production and refining have significant negative socio-ecological and environmental impacts [17, 18]. The petroleum hydrocarbons emitted from oil refining have a catastrophic impact on soil and aquatic ecosystems, leading to substantial disruptions in microbial processes and functions. It has been scientifically proven that pollution from petroleum products alters the soil and vegetation TPH and toxic metals levels, causes an increase in hydrocarbon-utilizing bacteria (HUB) and hydrocarbon-utilizing fungi (HUF) content of the soil and water, and hinders plants' nutritional values [9, 10, 19, 20]. Some of the most prevalent bacteria associated with petroleum pollution are *Staphylococcus, Mycobacterium, Streptococcus, Acinetobacter, Pseudomonas aeruginosa, and Rhodococcus.*

Additionally, *Aspergillus niger and Penicillium notatum* are predominant fungal species with the remarkable ability to utilize petroleum products [21, 22].

Aliphatic hydrocarbons, heavy metals (HMs), particulate matter, hydrogen sulfide (H₂S), carbon (ii) oxide (CO), nitrogen oxides (NOx), sulfur oxides (SOx), and soot are commonly associated with crude oil production and refining [10, 23]. An increase in the HMs, NOx, and sulfur SOx levels in the air is one of the possible causes of acid rain [24], which has significant environmental and engineering implications. Suspended water molecules have the ability to capture (absorb) HMs from atmospheric air, contaminating water vapor in the process, eventually resulting in the pollution of surface water bodies when these contaminated water droplets coalesce and fall to the ground [25]. Additionally, the presence of petroleum hydrocarbons in atmospheric water vapor increases the total petroleum hydrocarbon (TPH) levels in precipitation water [10, 26, 27], which alters the water's electrical and biological properties, leading to cascading effects on the ecosystems [28]. Waters' electrical conductivity (EC) has a significant impact on telecommunication services regarding signal attenuation, electromagnetic interference, transmission distances, and ground-penetrating radar capabilities [29].

Artisan (illegal) crude oil refining has become a significant challenge in many crude oil-producing nations, largely due to widespread corruption in these countries [26, 30-32]. In addition to producing subpar fuels that are detrimental to internal combustion engines, the local refineries operated by artisans also generate massive amounts of toxic gaseous emissions and hazardous waste materials, posing significant environmental and health concerns [18, 31]. Seepage from waste materials generated by these illegal refineries increases the potential toxic metal (PTM) concentration in soil and water [17, 23, 32]. Emissions from oil production and refining activities have been associated with the depletion of the atmospheric ozone level. This emission contains significant amounts of CO₂, CH₄, and VOCs, which can degrade atmospheric ozone levels, ultimately causing a reduction in the stratospheric ozone (O₃) stratum [33]. Heavy metal pollution has adverse effects on human health, causing respiratory infections, nervous system disorders, heart, liver, and kidney damage, and cancer. Exposure to high

doses of arsenic (As), cadmium (Cd), chromium (Cr), and nickel (Ni) is known to have carcinogenic effects [1, 34, 35]. Furthermore, it has been noted that water bodies accumulate dissolved heavy metals primarily from contaminated watersheds and the underlying hydraulic conductive system, which allows these contaminants to seep into the water [15, 36].

Previous investigations have primarily focused on the effect of illegal refinery activities on localized vegetation, soil, sediments, and surface water bodies [17, 23, 30-32]. Therefore, there is a dearth of information on the effects of artisan oil refinery activities on atmospheric deposition and the resulting environmental degradation over a larger area. This study is necessary because an adequate understanding of the prospective dangers of carcinogenic and non-carcinogenic pollutants is crucial for implementing effective preventive measures. Consequently, the key goal of this research is to appraise the impact of artisans' petroleum refining operations on the air quality, precipitation water, and surface water of the oil-rich Niger Delta region of Nigeria.

Materials and Methods

Description of the Study Region

This research was conducted in the Nigeria Niger Delta region. This is one of the world's largest wetlands, characterized by its rich mangrove and rain forests, as well as numerous slow-flowing streams and rivers. This region is not only significant for its ecological diversity but also for its substantial crude oil reserves [18]. Most of the streams in the coastal areas empty their contents into the rivers found in the region. The rivers in the region, such as the Niger River and its numerous tributaries, empty their waters into the Atlantic Ocean. This extensive network of highly interconnected waterways contributes to the region's rich biodiversity and complex ecosystem. Crude oil exploration is the major industrial activity in the region's wetlands, which has created environmental degradation through oil spills and gas flaring [31]. The upland region of the Niger Delta is also a key area for agricultural production and medium-scale industrial activities.

In addition to conventional crude oil production, the region also suffers from numerous illegal oil mining activities. These illegal (artisanal) refineries, often located in clusters along coastal areas, contribute significantly to environmental degradation [30]. Their waste products are typically deposited directly into swampy forests without proper treatment, resulting in further pollution of the region's water sources, air, soil, and vegetation. Within the past decade, the government has waged a significant war against these illegal refineries, leading to the destruction of thousands of makeshift structures. Since these refinery structures are being fabricated with locally available materials, they are easily rebuilt and made functional again [17, 32].

Information obtained from the Delta State University of Science and Technology revealed that the region has a rainfall volume of about 2400 mm annually and a temperature of 27±6ºC.

Experimental Setup

The experimental setup involved these basic steps: location selection (regions with high, medium, and low incidence of artisanal crude oil refining), sample collection (air and water), and a timeframe of the sampling (seasonally) to account for temporal variations in contamination levels. These are followed by laboratory analysis (in triplicates) of the samples collected from all the sites, data analysis using statistical methods (ANOVA) to validate the findings and establish the significance of the results, and result comparisons to international safety standards to evaluate their toxicity levels and potential risks.

Sample Collections

To facilitate a detailed analysis of the research, the Niger Delta region was categorized into three distinct sub-regions: high, medium, and low incidence zones, reflecting the varying degrees of illegal refinery activities in each area. The high-incidence areas (high-emission zones or Zone A) are the hotspots of illegal crude oil refining, characterized by strong evidence of extensive clusters (mostly destroyed) of these artisanal refineries. These areas witness the frequent destruction of artisanal refineries by law enforcement agencies. Also, these areas have a strong prevalence of water pollution, largely attributed to the reckless and illegal activities of oil criminals who exploit the local and global oil market. The low-incidence sub-regions (low-emission zones or Zone C) are areas with no significant history of artisanal petroleum refineries. These areas are primarily located in the upland regions, where the environmental impact of illegal oil mining activities is nonexistent. The medium incidence areas (medium-emission zones or Zone B) are regions where illegal crude oil refining activities are present but at a lower level compared to those in Zone A, where higher volumes of illegal refining operations are found.

Water Sampling

A total of 198 water specimens were sampled, comprising 90 rainwater (RW) samples and 108 surface water (SW) samples, for the purpose of this investigation. In each sub-region, 36 SW samples and 30 RW samples were collected, with sampling occurring at a rate of three times per month. The sampling of rainwater was not feasible during January or December due to insufficient rainfall. The samples were collected between January 2023 and December 2023, and the year was subdivided into two sections (seasons). The first experimental season was set between January 2023

and June 2023, while the second experimental season was set between July 2023 and December 2023.

Rainwater was harvested directly during downpours into plastic buckets placed on a platform 2 m above the ground and about 200 m from any high-rise features. Surface water samples were collected from major streams and rivers. In the high and medium-emission zones, priority was given to surface water bodies within the vicinity of abandoned illegal refineries. Both atmospheric rainwater and surface water samples were poured into sterilized amber glass bottles, coded, placed in ice-cooled containers, and transported to the laboratory immediately for analysis. During surface water sampling, precautions were taken to avoid disturbing the sediment at the bottom of the water body.

Air Quality Sampling and Measurement

A portable gas detector (model GC310, manufactured by Henan Chicheng Electric Co., Ltd. in China) was used to measure gaseous emissions in the region. Sampling was conducted at a height of approximately 2 m over a period of 1 hour. All the sampling points in the study were selected from areas with low traffic density. This approach was taken to ensure that high emissions from vehicular activities would not interfere with the sampling results, thereby maintaining the integrity and focus of the research.

Quality Assurance and Control

All the chemicals used in this work were of excellent rating (produced by Merck KGaA in Germany), while distilled water was used for the analysis. Blank and standard samples were analyzed using the same procedure. The tests were performed in triplicate, yielding a relative standard deviation of less than 4%, with recovery percentages for the certified reference materials ranging from 93.7% to 102.5%.

Laboratory Analyses

Water Potentially Toxic Metals (PTMs) Concentration

The PTM (arsenic "As", barium "Ba", cadmium "Cd", lead "Pb", nickel "Ni", copper "Cu", vanadium "V", mercury "Hg", and zinc "Zn") levels in water samples were determined using ASTM-approved guidelines. The water samples were sieved with Whatman filter paper. 10 mL of sieved water was carefully mixed with 50 mL of a combination of concentrated nitric acid and H_2O_2 in a specific ratio of 4 parts nitric acid to 1 part H_2O_2. The mixture was heated at 85ºC until it reached a clear state. Afterward, the solution was cooled to 27ºC, filtered into a cylinder, and then diluted to 100 mL with distilled water. An atomic absorption spectrophotometer (model AA-7800 series, manufactured in Japan) was used to measure each metal concentration in the digested water sample [11, 15]. Blank samples were

employed to guarantee the reliability and consistency of the results, and each test was conducted in triplicate, thereby verifying the accuracy and precision of the findings.

Total Petroleum Hydrocarbon (TPH)

Soxhlet extraction and liquid-liquid techniques were used to extract total petroleum hydrocarbons from water samples. 200 mL and 50 mL of dichloromethane were mixed together inside a sterilized separating funnel and shaken vigorously for 10 minutes. The aqueous phase was allowed to separate from the mixture, leaving an organic substance. This organic substance was poured into a calibrated container, diluted with 10 mL of CH_2Cl_2, and the resultant fractions were concentrated using a rotary concentrator. The extracted petroleum hydrocarbons from the water were quantified using gas chromatography, which was fortified with the flame ionization detector (GC-FID). The system has an HP-5 fused silica capillary (30 m×0.32 mm×0.25 µm) column, with a carrier gas (He) flowing at a slow rate of 1.75 mL/min, with the detection limit greater than 0.0001. 2 µL of the extract was introduced into the splitless mode at 250ºC, while the FID temperature was 300ºC. Initially, the column temperature was held at 50ºC for 2 minutes before it was increased to 250ºC at the rate of 10ºC per minute. The final results were analyzed using Agilent software [26].

Microbiological Analysis

The hydrocarbon-utilizing bacteria (HUB) and fungi (HUF) loads in the sampled RW and SW were determined in accordance with standard guidelines as explained by Achife [21].

Electrical Conductivity (EC)

The water EC was measured using a digital water electrical conductivity meter (Model S23030019034, manufactured by Mettler Toledo in Vietnam) at a temperature of 25ºC.

Dielectric Constant (ε′)

The ε' level of the water was measured at 25ºC with a frequency of 1 MHz using the capacitive technique with the aid of the capacitance and resistance (LCR) meter (model LCR-6002, Taiwan), following the procedures explained by Šegatin [37]. The water temperature (25ºC) was precisely monitored during the experimental procedure with the aid of a high-precision water bath (Model HH-4, produced by Hayat Scientific–Jordan). Equation (1) was used to calculate the water ε'.

$$\varepsilon^` = \frac{C_{ps}}{K_c} \tag{1}$$

Where C_{ps} = the water sample parallel capacitance corrected for 'stray' capacitance and K_c = mean cell constant [37].

Potential Toxic Metals (PTMs) Risk Assessment

Human beings primarily acquire water toxicity through oral and dermal exposure pathways. The health risks associated with the PTMs were analyzed based on carcinogenic and non-carcinogenic risk levels.

Average Daily Intake (ADI)

The ADI values of the PTMs in rainwater and surface water for non-carcinogenic risks were computed through Equations (2-3) [2, 5].

$$ADI(ing) = \frac{C \times I_{inh}R \times EF \times ED}{BW \times AT} \times CF \quad (2)$$

$$ADI(dem) = \frac{C \times SA \times AF \times ABS \times EF \times ED}{BW \times AT} \times CF \quad (3)$$

Similarly, the life average daily dose for carcinogenic risk (LADD) of the PTMs was computed through Equations (4-5) [2, 14].

$$LADD(ing) = \frac{C \times I_{inh}R \times EF \times ED}{BW \times AT} \times CF \quad (4)$$

$$LADD(dem) = \frac{C \times SA \times AF \times ABS \times EF \times ED}{BW \times AT} \times CF \quad (5)$$

Where ADI_{ing} is the ADI for the non-carcinogenic PTMs acquired through the oral pathway, ADI_{dem} is the ADI for the non-carcinogenic PTMs acquired through the dermal pathway, $LADD_{ing}$ is the ADI for the carcinogenic PTMs acquired through the oral pathway, and $LADD_{dem}$ is the ADI for the carcinogenic PTMs acquired through the dermal pathway. Additionally, C = concentration of the PTM, $I_{ing}R$ = the water ingestion rate (1.8 L for children and 2.0 L for adults), EF = exposure frequency, ED = exposure duration, BW = body weight (children ~35 kg and adults ~75 kg), AT = average contact time (ED x 365 for non-carcinogenic PTM and 75 x 365 for carcinogenic PTM), SA = skin surface area (children ~0.0028 m² and adults ~0.0057 m²), AF = adherence factor (0.2 and 0.07 mg cm⁻²day⁻¹ for children and adults, respectively), and ABS = dermal absorption factor, which is 0.001. CF is the conversion factor (0.001) used to homogenize the units from μg (units of the PTMs to mg kg⁻¹day⁻¹) standard unit of ADD and LADD [9, 14].

Non-Carcinogenic Risk

The non-carcinogenic risk of the PTMs was determined through the hazard quotient (HQ) and hazard index (HI), as calculated through Equations (6-8).

$$HQ_{ing} = \frac{ADI_{ing}}{RfD_{ing}} \quad (6)$$

$$HQ_{dem} = \frac{ADI_{dem}}{RfD_{dem}} \quad (7)$$

$$HI = \sum HQ_{ing} + \sum HQ_{dem} \quad (8)$$

Where RfD = Reference dose, the RfD_{ing} values for Cu, Pb, Zn, and Hg = 0.04, 0.0035, 0.3, and 0.0003 mg kg⁻¹ day⁻¹, respectively, while the RfD_{dem} values for Cu, Pb, Zn, and Hg = 1.2x10⁻², 5.25x10⁻⁴, 6.0x10⁻², and 2.1x10⁻⁵ mg kg⁻¹ day⁻¹, respectively [14].

Carcinogenic Risk

The PTM carcinogenic risk factor was calculated through Equations (9-11).

$$CR_{ing} = LADD_{ing} \times SF_{ing} \quad (9)$$

$$CR_{dem} = LADD_{dem} \times SF_{dem} \quad (10)$$

$$TCR = \sum CR_{ing} + \sum CR_{dem} \quad (11)$$

Where SF_{ing} is the ingestion (oral) cancer slope factor for the PTMs (Ni = 1.7, Cd = 6.1, and As = 1.5 kg day mg⁻¹), SF_{dem} = dermal cancer slope factor with Ni, Cd, and As, with values of 0.2, 6.1, and As = 3.66 kg day mg⁻¹, respectively [14].

Statistical Analysis

The data obtained were subjected to descriptive statistics. Analysis of variance (ANOVA) was conducted on the results to evaluate the significance of illicit refinery operations on the air and water quality. Also, the mean values obtained were separated using the Duncan's Multiple Range Test (DMRT) at p≤0.05. All the tests were done in three replications, and the mean results were documented.

Results and Discussion

Total Petroleum Hydrocarbons and Potential Toxic Metals (PTMs) Levels

Tables 1 and 2 show the descriptive statistics of the total petroleum hydrocarbons (TPH) and PTM levels in rainwater (RW) and surface water (SW) harvested from the region during the two experimental seasons. In the first experimental season, the harvested RW-recorded TPH concentrations were 57.00, 28.2, and 16.67 μg/L in the high, medium, and low-emission zones, respectively. During the second experimental period, the TPH level in the rainwater was 58.93, 29.67, and 16.73 μg/L at the high, medium, and low-emission zones, respectively.

With respect to the RW metals content, during the first and second sampling seasons, rainwater Ni concentrations varied from BDL to 9 µg/L and BDL to 8 µg/L, respectively. Cu levels varied from 8 to 40 µg/L and 11 to 38 µg/L, respectively; Pb concentrations ranged from BDL to 4 µg/L and BDL–5 µg/L,

Table 1. The TPH and PTMs levels in rainwater.

	First season			Second season			WHO*
	High emission	Medium emission	Low emission	High emission	Medium emission	Low emission	
TPH (µg/L)	57.00^c±20.44 (27–81)	28.2^b±6.94 (19–37)	16.67^a±6.26 (7–27)	58.93^c±17.49 (32–84)	29.67^b±7.02 (12–46)	16.73^a±5.82 (9–26)	
Ni (ppb)	3.80^c±3.25 (BDL–9)	2.27b±2.46 (BDL–7)	1.73^a±1.59 (BDL–4)	3.33^c±2.27 (BDL–8)	2.20^b±2.38 (BDL–6)	1.27^a±1.28 (BDL–3)	20
Cu (ppb)	25.73^d±9.05 (12–40)	22.73^c±6.08 (13–30)	17.60^b±4.49 (8–23)	27.93e±4.22 (20–38)	24.33^d±4.62 (15–32)	15.13^a±3.80 (11–21)	200
Pb (ppb)	1.00^d±1.42 (BDL–4)	0.47^b±0.69 (BDL–3)	0.33^a±0.58 (BDL–3)	1.27^c±1.88 (BDL–5)	0.53^c±0.77 (BDL–4)	0.33^a±0.58 (BDL–2)	10
Cd (ppb)	0.67^c±0.65 (BDL–4)	0.20^c±0.34 (BDL–1)	0.07^a±0.12 (BDL–1)	0.60^c±0.92 (BDL–3)	0.33^d±0.43 (BDL–2)	0.13^b±0.23 (BDL–1)	3
Zn (ppb)	38.33^d±11.39 (25–63)	23.60^b±6.68 (10–43)	17.87^a±3.28 (13–22)	36.27^c±10.62 (21–54)	22.87^b±5.45 (14–29)	18.53^a±3.99 (13–25)	500
As (ppb)	0.13^b±0.23 (BDL – 1)	BDL	0.13^b±0.23 (BDL – 2)	0.13^b±0.23 (BDL -1)	0.07^a±0.12 (BDL -1)	BDL	10
V	BDL	BDL	BDL	BDL	BDL	BDL	
Hg	BDL	BDL	BDL	BDL	BDL	BDL	
Ba	BDL	BDL	BDL	BDL	BDL	BDL	

Mean±standard deviation and range in parenthesis, Rows with the same superscript letter indicate that the values are not statistically significant from one another at p≤0.05 using DMRT, * = WHO Standards for Drinking Water [45].

Table 2. The TPH and PTMs levels in the surface water.

	First season			Second season			WHO*
	High emission	Medium emission	Low emission	High emission	Medium emission	Low emission	
TPH (µg/L)	561^d±228 (241–980)	372^b±71 (173–545)	100^a±41 (29–292)	503^c±81 (201–916)	339^b±96 (114–599)	99^a±21 (24–161)	
Ni (ppb)	6.87^d±5.32 (BDL–16)	5.60^d±4.77 (BDL–12)	4.07^c±2.88 (BDL–9)	8.20^c±6.69 (BDL–21)	3.26^a±2.35 (BDL–10)	3.87^b±2.97 (BDL–12)	20
Cu (ppb)	26.67^c±9.34 (12–40)	20.93^b±6.62 (10–33)	19.47^a±6.76 (9–31)	28.40c±8.71 (14–46)	22.73^b±6.98 (11–32)	19.13^a±7.09 (8–33)	200
Pb (ppb)	1.07^d±1.08 (BDL–2)	0.40^a±0.54 (BDL–3)	0.60^c±0.58 (BDL–3)	1.00^d±0.92 (BDL–4)	0.53^b±0.65 (BDL–3)	0.60^c±0.75 (BDL–3)	10
Cd (ppb)	0.80^d±1.23 (BDL–3)	0.53^b±0.78 (BDL–3)	0.33^a±0.35 (BDL–2)	0.80^d±1.11 (BDL–3)	0.53^b±0.62 (BDL–3)	0.60^c±0.77 (BDL–3)	3
Zn (ppb)	41.13^c±15.51 (20–70)	25.27^a±7.54 (13–25)	25.73^a±6.43 (17–38)	44.73^d±13.44 (21–90)	26.27^b±7.84 (14–43)	27.00^b±7.37 (15–40)	500
As (ppb)	0.40a±0.69 (BDL–3)	0.47^a±0.65 (BDL–4)	0.60^c±0.89 (BDL–3)	0.67^c±0.77 (BDL–3)	0.53^b±0.09 (BDL–3)	0.67^c±1.01 (BDL–5)	10
V (ppb)	BDL	BDL	BDL	BDL	BDL	BDL	
Hg (ppb)	0.20^b±0.35 (BDL–2)	0.13^a±0.23 (BDL–1)	0.20^b±0.35 (BDL–2)	0.13^a±0.23 (BDL–1)	0.20^b±0.34 (BDL–2)	0.27^c±0.46 (BDL–3)	6
Ba (ppb)	BDL	BDL	BDL	BDL	BDL	BDL	

Mean±standard deviation (range in parentheses), rows with the same common letter (superscript) indicate that they are not significantly differ at p≤0.05 using DMRT, * = WHO Standards for Drinking Water [45].

respectively; Cd concentrations ranged from BDL–4 μg/L and BDL–3 μg/L, respectively; Zn levels ranged from 10 to 63 μg/L and 13 to 54 μg/L, respectively; and As centration varied from BDL to 2 μg/L and BDL to 1 μg/L, respectively. It is noteworthy that vanadium, mercury, and barium metals were not found in the rainwater, regardless of the sampling period or duration.

Table 2 presents the TPH and PTM concentrations in the surface water sampled from the three experimental zones. It was noted that the surface water TPM levels during the first and second experiment seasons ranged from 29 to 980 μg/L and 24 to 916 μg/L, respectively. Additionally, during the first experimental period, the Ni, Cu, Pb, Cd, Zn, As, and Hg levels in the SW ranged from BDL–16 μg/kg, 9–40 μg/kg, BDL–3 μg/kg, BDL–3 μg/kg, 13–70 μg/kg, BDL–4 μg/kg, and BDL–4 μg/kg, respectively. Then, during the second experimental season, the surface water Ni, Cu, Pb, Cd, Zn, As, and Hg levels varied from BDL–21 μg/kg, 8–46 μg/kg, BDL–4 μg/kg, BDL–3 μg/kg, 14–90 μg/kg, BDL–5 μg/kg, and BDL–3 μg/kg, respectively. The analysis showed that Cu and Zn were the most predominant PTMs in the SW, with extremely low levels of Hg, Cd, and As also present. The order of PTM concentrations in the RW and SW was Zn>Cu>Ni>Pb>Cd>As and Zn>Cu>Ni>Pb>Cd>As>Hg, respectively. Generally, SW had higher PTM contents when compared to rainwater, depicting that additional natural and anthropogenic factors, such as soil mineral content, natural weathering, and industrial discharges, contributed to the elevated surface water PTM levels [32, 38].

Specifically, the results indicated that the TPH levels in water samples (SW and RW) from the high-emission zone were noticeably higher than those from the other two zones. This indicates that illegal crude oil refinery operations have a substantial impact on the TPH of harvested rainwater and surface water. This is in agreement with previous findings of Refs. [10, 26], which stated that crude oil refining releases substantial amounts of hydrocarbons into the environment, which can dissolve into atmospheric water molecules and ultimately lead to increased TPH levels in precipitation water. The trace of TPH detected in the upland area (Zone C) SW, despite the absence of illegal refinery activities, could be attributed to accidental petroleum product spills from marine vessels and seepage from carelessly discarded petroleum products. According to Uguru [9], accidental spills from maritime operations can contribute immensely to water bodies' pollution by increasing the hydrocarbons and PTM levels. The TPH levels in SW and RW observed in this study were lower than those reported by [29, 32] but higher than the results found by [10] in their investigations on the impacts of oil spills on water bodies.

Furthermore, aside from the elevated TPH levels in water samples from the high-emission zone (Zone A), their PTM levels were consistently greater than those documented for the other two (B and C) zones. This

affirmed previous scientific reports [10, 17] that petroleum products have the capacity to increase the concentration of metals in water, posing potential environmental and health risks.

The results revealed that the Zn, Pb, Ni, and Cu recorded in this study's RW and SW were lower than the values recorded by [11, 32, 38, 39] for surface waters. In contrast, the Pb, Zn, and Cu levels in the RW and SW were higher than the values reported by Okey-Wokeh [40], and this study's water samples had Hg content greater than the value obtained by Acioly [8]. The varying levels of metal concentrations in water reported by different researchers may be attributed to differences in the types of pollutants (anthropogenic influences), sampling timing, precipitation volume, and experimental errors [8, 11]. Anthropogenic activities such as poor waste management and poor farming practices can deposit toxic metals in the environment, which can seep directly into water bodies [9]. Interestingly, the mean heavy metal levels in SW and RW were below the maximum allowable limits recommended by WHO/FAO for drinking water.

Remarkably, some of the HM (Zn, Hg, and As) levels in the low-emission zone SW were significantly greater than the results obtained from the medium-emission zone. This could be attributed to seepage from industrial activities, domestic wastes, and agricultural chemicals into the water bodies [41, 42] since effluents from electronic waste and agricultural chemicals are rich in Hg, Pb, As, Cd, Zn, and Cu [36, 38, 43]. Runoffs from industrial regions are usually rich in As, Hg, Zn, and Pb, which are often deposited in natural water bodies [15, 44]. In the Niger Delta region, agricultural activities and small to medium-scale industrial activities predominantly occur in the upland; therefore, the indiscriminate disposal of waste materials can lead to the toxicity of these potentially toxic elements in the environment. Arsenic toxicity has been associated with cardiovascular diseases, cancer, and diabetes, while chronic exposure to cadmium can lead to various forms of cancers, kidney damage, bone demineralization, and respiratory issues [6]. Protracted exposure to lead can result in significant health risks, including the potential for neurological damage, cardiovascular problems, kidney damage, and reproductive complications. Additionally, nickel toxicity has been linked to lung cancer, respiratory issues, and skin irritation [35].

Atmospheric Air Quality

Table 3 presents the air quality of the study region. It was noted the highest and lowest VOC, SO_2, CH_4, NO_2, CO, and NH_3 levels were recorded in the high-emission and low-emission zones, respectively, while the highest O_3 value was recorded in the low-emission zone. During the first experimental season, the O_3, VOC, SO_2, CH4, NO_2, CO, and NH_3 values ranged from 0.03 to 0.15 ppm, 3.11 to 11.02 ppm, 1.54 to 8.47 ppm, 2.0 to 23.00 ppb, 9.0 to 42 ppb, 15.0 to 52.00 ppb, and 1.01 to 2.84 ppm,

Table 3. The air quality result.

Parameter	First season			Second season			WHO*
	High	Medium	Low	High	Medium	Low	
Ozone (ppm)	0.06±0.02 (0.03–0.09)	0.08±0.02 (0.03–0.13)	0.12±0.05 (0.04–0.15)	0.06±0.02 (0.02–0.10)	0.07±0.03 (0.03–0.13)	0.11±0.03 (0.06–0.15)	0.07
VOC (ppm)	8.71±1.36 (6.09–11.02)	6.85±1.65 (4.65–9.93)	5.12±0.84 (3.11–6.36)	8.36±0.88 (6.33–10.6)	5.55±1.89 (3.11–10.39)	4.52±0.76 (3.06–6.22)	NA
CH_4 (ppm)	6.89±1.13 (5.06–8.47)	4.96±1.06 (3.95–7.15)	2.80±0.58 (1.54–3.95)	7.18±1.12 (5.22–9.37)	5.09±1.51 (2.29–7.76)	3.10±0.91 (1.96–4.64)	NA
SO_2 (ppb)	17.17±2.46 (13.0–23.00)	11.90±2.99 (7.0–18.00)	5.78±1.71 (2.0–10.00)	18.11±2.97 (12.0–23.0)	12.17±2.80 (8.0–19.00)	7.45±2.66 (3.0–12.00)	190
NO_2 (ppb)	31.83±6.92 (22.0–42.00)	22.67±5.33 (12.0–31.0)	18.00±4.09 (9.0–25.00)	32.22±5.30 (25.00–44.0)	26.50±4.06 (20.00–35.0)	19.89±4.17 (13.00–31.0)	106
CO (ppb)	34.78±7.85 (17.0–52.00)	29.39±6.96 (20.0–41.0)	23.78±7.12 (15.0–40.0)	37.39±7.87 (20.0–55.0)	30.72±7.68 (19.0–44.00)	26.28±8.41 (15.0–40.0)	8700
NH_3 (ppm)	2.18±0.43 (1.55–2.84)	1.74±0.28 (1.21–2.55)	1.36±0.33 (1.01–2.24)	2.77±0.42 (1.75–3.51)	1.74±0.34 (1.17–2.35)	1.42±0.52 (0.66–2.45)	NA

*WHO maximum allowable limit [3], Mean±standard deviation (range in parentheses).

respectively. Then, during the second experimental season, it was observed that the atmospheric air O_3, VOC, SO_2, CH_4, NO_2, CO, and NH_3 values varied from 0.02 to 0.15 ppm, 3.06 to 10.60 ppm, 1.96 to 9.73 ppm, 3.0 to 23.00 ppb, 13.00 to 44.00 ppb, 15.0 to 55.00 ppb, and 0.66 to 3.51 ppm, respectively. Generally, the concentration of the VOCs, SO_2, CH_4, NO_2, CO, and NH_3 recorded at the high-emission zone almost doubles the results documented for the low-emission zone. This shows that anthropogenic activities, probably rampant emissions from illegal oil refineries, likely contribute to the sudden increase in toxic gases in the air, posing a significant environmental concern.

The lower levels of O_3 and the high concentrations of NOx and VOCs recorded in zone A could contribute to ozone layer depletion, resulting in severe negative effects on the region's ecosystems. Low O_3 levels can reduce the stratosphere layer's protective effect, creating ecosystem imbalance and exacerbating climate change effects [33]. Furthermore, the presence of NO_2, SO_2, and CO in the zone with high emissions will play a significant role in the formation of acidic rain [46], which has numerous detrimental effects on both human health and ecosystems. In addition to the formation of acid rain, excessive exposure to high concentrations of CO, NO_2, and NH_3 can also cause serious health problems, including optical problems, cardiovascular problems, impaired brain function, and disorders of the respiratory system [47].

In addition to the gases emitted during the combustion processes involved in crude petroleum refining, the evaporation of volatile hydrocarbons and other compounds from petroleum product spills, which are highly associated with artisan refineries, plays a significant role in atmospheric contamination. These evaporative emissions lead to the release of total petroleum hydrocarbons (TPH), toxic gases like volatile organic compounds (VOCs), and even metals into the atmosphere [17, 30]. Although the concentrations of O_3, NO_2, CO, and SO_2 across the region were generally below the maximum WHO-approved limits for air pollutants, the high pollutant levels detected at the high-emission zones underscore the need for robust air quality monitoring. This highlights that, in addition to reducing emissions from crude petroleum refining systems, measures should also be implemented to decrease emissions from agricultural, transportation, and industrial activities. Anthropogenic activities related to conventional agriculture and industrial activities are key factors contributing to air pollution and climate change issues [2, 6]. Therefore, by addressing these pollution sources, emissions from a broader range of sources will be reduced, leading to more significant progress in mitigating climate change.

Microbiological and Electrical Properties of the Water

The results of water microbial and electrical property values are presented in Table 4. Generally, the HUB and HUF load in SW was significantly higher than the population recorded in the RW. The HUB load in RW and SW varied from $0–10\times10^3$ and 2 to 59×10^3 cfu/mL, respectively. Likewise, the HUF population in the RW and SW varied from $0–29\times10^3$ cfu/mL and $1–33\times10^3$ cfu/mL, respectively. The data from Table 4 showed significant variations in HUB and HUF loads across the region, with Zone A recording the highest population and Zone C the lowest population. Consistent with the findings of Ref. [21], our study reveals that the presence of petroleum hydrocarbons in water bodies (SW and TW) leads to a substantial increase in the HUB and HUF population. This echoes similar observations made by the previous study [21].

Table 4. The microbial load and electrical properties of the rain and surface water.

	Source	First season			Second season		
		High	Medium	Low	High	Medium	Low
		Microbiology					
HUB	RW	2.33c±2.42 (0–8)	2.17b±2.07 (0–6)	1.61a±1.64 (0–7)	3.56d±3.98 (0–10)	2.00b±2.23 (0–8)	1.44a±1.47 (0–5)
	SW	29.44^c±17.1 (12–59)	22.94^b±10.49 (9–46)	13.39^a±6.01 (4–28)	31.33^d±11.84 (14–56)	21.61^b±8.18 (7–48)	12.61^a±6.53 (2–31)
HUF	RW	1.94^c±1.63 (0–5)	1.52^b±1.68 (0–4.5)	1.15^a±1.38 (0–4.3)	2.43^d±2.01 (0–6)	1.44^b±1.35 (0–7)	1.28^a±1.15 (0 –5.7)
	SW	15.17d±4.02 (5–28)	11.22^c±5.87 (1–22)	5.67^a±3.36 (1–16)	16.87^d±5.59 (5–33)	9.47^b±4.74 (2–18)	5.33^a±3.19 (1–11)
		Electrical					
ε′	RW	49.06^a±4.47 (38–57)	54.78^b±4.89 (46–66)	69.39^d±4.33 (56–75)	50.83^a±4.51 (41–60)	55.61^b±4.45 (46–65)	70.94^d±2.76 (64–79)
	SW	36.33^a±4.92 (29–44)	44.06^b±6.31 (31–53)	52.22^c±3.08 (46–61)	36.94^a±4.12 (27–49)	45.05^b±5.51 (37–55)	53.17^c±3.85 (46–64)
EC	RW	51.67^a±7.35 (39–67)	60.94^b±11.07 (44–84)	66.83^c±9.65 (52–91)	53.50a±5.04 (44–65)	61.56^b±12.3 (45–89)	66.06^c±8.02 (51–82)
	SW	578.22^a±116 (387–765)	624.00^b±67 (434 –854)	702.06^c±142 (512–993)	546.72^a±79 (332–766)	638.56^b±104 (423–792)	688.22^c±129 (482–936)

Mean±standard deviation (range in parentheses), rows with the same common letter (superscript) indicate that they are not significantly differ at p≤0.05 using DMRT.

Interestingly, the HUB and HUF levels recorded in this study were consistently lower than those reported by [22] for other regions' petroleum-polluted surface water. On the contrary, this study's HUB and HUF levels were lower than the findings of Ntongha [48] on experimental investigation of oil-contaminated environments. Petroleum-utilizing microbes play an essential role in the bioremediation of hydrocarbon toxins, leading to a safer environment; however, their high pollution can create biodiversity imbalances [19].

Electrical Properties

Dielectric Constant (ε′)

The ε′ values obtained for SW and RW specimens and presented in Table 4 indicated that the oil pollution had a substantial impact on the water's electrical properties. During the first experimental period, RW and SW ε′ values in the high-emission zone ranged from 38–57 and 29–44, respectively; in the medium-emission zone, the ε′ values ranged from 46–66 and 31–53 in the RW and SW, respectively; and in the low-emission zone, the RW and SW ε′ values ranged from 56–75 and 46–61, respectively. Then, in the second experimental season, the RW ε′ values varied from 41–60, 46–65, and 64–79 at the high, medium, and low-emissions zones, respectively, while the SW ε′ values varied from 27–49, 37–55, and 46–64 in Zones A, B, and C, respectively. The lower ε′ values were recorded at Zone A compared to Zone C and can be linked to the high concentration

of oil in the sub-region's water. Oil is a non-polar liquid, which has the ability to disrupt hydrogen bonding between water molecules, leading to a reduction in the oil-polluted water dielectric constant [49].

Furthermore, the results of the experiment showed that the ε′ values of rainwater were significantly higher than those of surface water. This can be attributed to the higher concentrations of dissolved salts and other impurities in surface water, which contribute to an increment in ionic conductivity or other complex interactions of water [50]. Water ε′ has several implications for electrical engineering, telecommunications, and environmental monitoring. According to Amajama [51], low water ε′ values have negative implications on telecommunication services, affecting the reflection and refraction of electromagnetic waves, causing alteration in the signal propagation paths, and consequently affecting network signal strength and quality. Therefore, the lower ε′ values of the region's SW may likely interfere with telecommunication services, remote sensing, and radar system services in the area, potentially causing disruptions or outages.

Electrical Conductivity (EC)

The results of RW and SW electrical conductivity revealed that the sampling location had a significant effect on the water EC value. The first experimental period saw RW recording mean EC values of 51.67, 60.94, and 66.83 μs/cm at Zones A, B, and C, respectively, while SW developed average EC values of

578.22, 624.00, and 702.06 µs/cm at Zones A, B, and C, respectively. Then, in the second experimental period, RW samples from the high, medium, and low-emission zones showed mean EC values of 53.50, 61.56, and 66.06 µs/cm, respectively, while SW samples from the same zones had average EC values of 546.72, 638.56, and 688.22 µs/cm, respectively. This finding revealed Zone A consistently exhibited the lowest EC values, regardless of the water source, which can be attributed to the high levels of petroleum hydrocarbons present in Zone A water, giving it an oily nature (Table 2). Due to oil's lower electrical conductivity, it creates a barrier around water molecules, forming insulating layers that impede the flow of electric current. This results in an increase in water resistance and decreased conductivity [29].

These research EC values were lower than the results obtained for other crude oil-impacted surface water [52]. According to USEPA [53], spills from petroleum and its derivatives have the ability to lower water's electrical conductivity. In addition to the lower oil volume in Zone C water, the soil types and leachates from industrial and agricultural activities could be responsible for the elevated EC values recorded in this zone. Water that flows through clay soils that contain organic materials tends to have higher EC, as these increase the concentration of electrolytes in water [53]. Lower electrical conductivity reduces the availability of dissolved calcium, magnesium, sodium, and chloride ions, which are crucial for the growth and development of aquatic organisms. Additionally, lower conductivity presents significant challenges in water treatment and remediation processes, making the water susceptible to pH fluctuations [28]. The water in Zone A exhibits a unique property, as it can slow down the degradation of electromagnetic waves, which is attributed to its lower electrical conductivity [54]. This enhances more effective transmissions and telecommunication signal reception, ultimately improving the integrity of telecommunications services.

Health Risks Associated with Water Intake

Non-Carcinogenic Risk

The results of the non-carcinogenic hazards associated with exposure to water samples are presented in Table 5. The study showed that children are more susceptible to the risks, with a higher level of exposure and sensitivity compared to adults. According to the non-carcinogenic risk calculations, the ADI_{dem} exposure values indicated lower mean levels compared to the ADI_{ing} exposure values. It was noted that in rainwater, the average daily dose of the PTMs followed a specific order of Pb<Zn<Cu. In contrast, in SW, the order of PTMs' average daily dose concentrations was Hg<Pb<Cu<Zn. In addition, the ADI values obtained in the high-emission zone were found to be considerably higher

Table 5. The ADI (mg/kg.d), HQ and HI of the rainwater and surface water.

Metal	Source	Emission level					
		High		Medium		Low	
		Children	Adult	Children	Adult	Children	Adult
		ADI_{ing} (x10^{-4})**					
Cu	RW	13.800	7.1500	12.100	6.270	8.420	4.370
	SW	14.200	7.3400	11.200	5.820	9.930	5.150
Pb	RW	0.581	0.3010	0.257	0.133	0.169	0.0880
	SW	0.530	0.2750	0.242	0.125	0.309	0.160
Zn	RW	19.400	10.000	11.900	6.190	9.360	4.85
	SW	22.100	11.400	13.300	6.870	13.600	7.03
Hg	SW	0.0874	0.0453	0.0874	0.0453	0.118	0.0613
		ADI_{dem} (x10^{-5})**					
Cu	RW	42.900	14.30	37.600	12.500	26.200	8.710
	SW	44.000	14.60	34.900	11.600	30.900	10.300
Pb	RW	1.810	0.601	0.800	0.266	0.528	0.176
	SW	1.650	0.548	0.752	0.250	0.960	0.319
Zn	RW	60.200	20.000	37.200	1.24	2.91	9.68
	SW	68.700	22.800	41.200	13.700	42.200	14.000
Hg	SW	0.272	0.0904	0.272	0.0904	0.368	0.122

		HQ$_{ing}$ (x10^{-3})**					
Cu	RW	34.50	17.90	30.30	15.70	21.10	10.90
	SW	35.50	18.40	28.00	14.60	24.80	12.90
Pb	RW	16.6	8.60	7.34	3.80	4.83	2.51
	SW	15.10	7.86	6.91	3.57	8.83	4.57
Zn	RW	6.47	3.33	3.97	2.06	3.12	1.62
	SW	7.37	3.80	4.43	2.29	4.53	2.34
Hg	SW	102.00	52.70	102.00	52.70	137.00	71.30
		HQ$_{dem}$ (x10^{-2})**					
Cu	RW	3.580	1.190	3.130	1.040	2.180	0.726
	SW	3.670	1.220	2.910	0.967	2.580	0.858
Pb	RW	3.450	1.140	1.520	0.507	1.010	0.335
	SW	3.140	1.040	1.430	0.476	1.830	0.608
Zn	RW	1.000	0.333	0.620	0.207	0.485	0.161
	SW	1.150	0.380	0.687	0.228	0.703	0.233
Hg	SW	3.160	1.050	3.160	1.050	4.280	1.420
		HI (x10^{-2})**					
HI$_{ing}$	RW	5.76	2.98	4.16	2.16	2.91	1.50
	SW	16.00	8.28	14.10	7.32	17.50	9.11
HI$_{dem}$	RW	8.03	2.66	5.27	1.75	3.68	1.22
	SW	11.10	3.69	8.19	2.72	9.39	3.12
		ΣHI**					
	RW	1.38x10^{-1}	5.64x10^{-2}	9.43x10^{-2}	3.91x10^{-2}	6.59x10^{-2}	2.72x10^{-2}
	SW	2.71x10^{-1}	1.20x10^{-1}	2.23x10^{-1}	1.00x10^{-1}	2.69x10^{-1}	1.22x10^{-1}

RW = Rainwater, SW = Surface water, ** = average value of the two sampling periods.

than those measured in the medium and low-emission zones. This notable disparity in water pollution levels across the three zones could be attributed to higher effluent discharge from illegal oil refining activities in the high-risk zones [9].

The health hazard quotient and index (HQ and HI) of the water, through ingestion and dermal exposure routes (Table 5), indicated that the sampling region and period had a substantial effect on the non-carcinogenic levels of potentially toxic metals (PTMs). SW generally had higher HQ values than RW, which can be attributed to the higher PTM levels in SW (Tables 1 and 2). Although Cu and Hg contribute significantly to the non-cancerous health risk associated with hazardous metals, the HI values for SW and RW were found to be within the internationally acceptable limits (HI<1). According to the World Health Organization, if HI value exceeds 1 (HI>1), it is essential to consider possible non-carcinogenic health threats (diseases) linked with prolonged exposure to the substance in question for human populations [14]. The HQ and HI values detailed

in this study were within the range reported by Ref. [8] for other surface water bodies but greater than the results documented by previous researchers [11].

Carcinogenic Risk (CR)

The CR results of rainwater and surface water samples are presented in Table 6. Regardless of the exposure pathway and the PTM, the CR values of surface water were generally greater than the values recorded for rainwater. The high-emission zone specifically had the maximum CR$_{ing}$ and CR$_{dem}$ values. Individually, the CR values followed this increasing pattern, As>Cd>Ni, signifying that As had the least carcinogenic and Ni had the maximum carcinogenic potential in both rainwater and surface water samples. Additionally, it was noted that oral exposure (ΣCR$_{ing}$) presented a greater carcinogenic risk than the dermal pathway (ΣCR$_{dem}$). Based on the TCR results, its value ranged from 9.69x10^{-5} to 6.53x10^{-4} in RW and 3.35x10^{-4} to 1.08x10^{-3} in SW, with the water sampled from

Table 6. The carcinogenic risk of the rainwater and surface water.

PTM	Source	High		Medium		Low	
		Children	Adult	Children	Adult	Children	Adult
CDI_{ing} ($\times 10^{-5}$)**							
Ni	RW	1.84E-04	9.52	11.50	5.95	7.71	4.00
	SW	3.87E-04	20.10	22.80	11.80	20.60	10.70
Cd	RW	3.24	1.68	1.39	0.72	0.514	0.267
	SW	4.11	2.13	2.73	1.41	2.42E-05	1.25
As	RW	0.669	0.347	0.154	0.080	0.360	0.187
	SW	2.73	1.41	2.57	1.33	3.24	1.68
CDI_{dem} ($\times 10^{-5}$)**							
Ni	RW	5.71	1.90	3.57	1.19	2.40	0.798
	SW	12.0	4.01	7.09	2.36	6.40	2.13
Cd	RW	1.01	0.335	0.432	0.144	0.160	0.0532
	SW	1.28	0.426	0.848	0.282	0.752	0.250
As	RW	0.208	0.0692	0.0480	0.0160	0.112	0.0372
	SW	0.848	0.282	0.800	0.266	1.01	0.335
CR_{ing} ($\times 10^{-4}$)							
Ni	RW	3.13	1.62	1.96	1.01	1.31	0.680
	SW	6.58	3.42	3.88	2.01	3.50	1.820
Cd	RW	1.98	1.02	0.848	0.439	0.314	0.163
	SW	2.51	1.30	1.67	0.860	1.48	0.763
As	RW	0.100	0.521	0.0231	0.012	0.0540	0.0281
	SW	0.410	0.212	0.386	0.200	0.486	0.252
CR_{dem} ($\times 10^{-5}$)							
Ni	RW	6.240	2.080	3.880	1.290	1.570	0.522
	SW	2.400	0.802	1.420	0.472	1.280	0.426
Cd	RW	6.160	2.040	2.640	0.878	0.976	0.325
	SW	7.810	2.600	5.170	1.720	4.590	1.530
As	RW	0.761	0.253	0.176	0.0586	0.410	0.136
	SW	3.100	1.03	2.930	0.974	3.700	1.230
ΣCR ($\times 10^{-4}$)							
ΣCR_{ing}	RW	5.210	2.690	2.830	1.460	1.680	0.871
	SW	9.500	4.930	5.940	3.070	5.470	2.84
ΣCR_{dem}	RW	1.320	0.437	0.6700	0.223	0.296	0.0983
	SW	1.330	0.443	0.952	0.317	0.957	0.319
TCR ($\times 10^{-4}$)							
	RW	6.53	3.13	3.50	1.68	1.98	0.969
	SW	10.80	5.37	6.89	3.39	6.43	3.16

RW = Rainwater, SW = Surface water, **= average value of the two sampling periods.

the high-emission zone consistently recording the highest TCR value. Notably, this study's TCR values are in alignment with those values obtained for Sele River Estuary water [11].

These TCR results highlight the PTM's potential carcinogenic menace on human health through oral and dermal exposure pathways. As depicted by the TCR values, apart from the children who had prolonged exposure to SW in the high-emission zone, the PTM levels in the remaining zones are within the tolerable carcinogenic risk range, irrespective of the age bracket and water source. Tolerable carcinogenic risks for PTMs range from $1x10^{-6}$ to $1x10^{-4}$, while TCR values that are higher than $1x10^{-4}$ are considered unacceptable and have a greater risk of causing carcinogenic diseases [9, 14]. Therefore, children in the high-emission zone have a high probability of developing carcinogenic diseases through exposure to the region's surface water. The TCR values obtained in this study were generally less than the results documented by Ugwu [37] for surface water bodies but within the range of results stated by other researchers [42, 55] for some selected SW bodies from different geographical regions. A comprehensive understanding of the hazards posed by carcinogenic and non-carcinogenic pollutants is crucial for implementing effective preventive measures to safeguard public health.

Conclusions

This research was embarked upon to provide insights into the influence of artisanal oil refineries on atmospheric air and water quality. Air, rainwater (RW), and surface water (SW) samples were collected from both nearby and distant areas around crude petroleum refining clusters to assess potential environmental impacts. These samples were analyzed to evaluate their potential toxic metals (PTMs), total petroleum hydrocarbons (TPH), hydrocarbon-utilizing bacteria (HUB), hydrocarbon-utilizing fungi (HUF), electrical conductivity (EC), dielectric constant (ε'), and gaseous components. The outcomes indicate that environmental pollution led to an increase in TPH and PTM levels in both RW and SW, with TPH, Cu, Pb, As, Cd, Zn, and Hg contamination levels higher in SW compared to RW. Remarkably, the results highlighted that both RW and SW samples generally contained high Cu and Zn concentrations, with only trace amounts of Hg and Cd. Concerning air quality, the emissions from illegal oil refining activities increased the VOCs, SO_2, NO_2, CO, CH_4, and NH_3 levels and caused depletion of atmospheric ozone levels. Notably, the outcomes of this study revealed that artisanal oil refinery activities led to an increase in HUB and HUF levels, while there was a decrease in the EC and dielectric constant values in RW and SW samples. Regarding health risk assessment, HI values were below 1 (HI<1), which is the threshold indicating that exposure

to the PTMs cannot result in non-carcinogenic health hazards. Additionally, the carcinogenic risk was within the acceptable range for both SW and RW (TCR>$1x10^{-4}$), except for the SW in the high-emission zone, where children showed a higher risk level. These findings demonstrate that the activities of crude oil saboteurs have a significant impact on coastal regions, highlighting the necessity for thorough environmental monitoring of the oil-producing coastal areas.

Conflict of Interest

The authors declare no conflict of interest.

Notations and Nomenclature List

BDL = Below detection limit
CH_4 = Methane
CO = Carbon monoxide
Cu Copper
CR = Carcinogenic risk
HUB = Hydrocarbon-utilizing bacteria
HUF = Hydrocarbon-utilizing fungi
Pb = Lead
Hg = Mercury
NH_3 = Ammonia
NO_2 = Nitrogen dioxide
ppb =   Part per million
PTMs = Potential toxic metals
RW = rain water
SO_2 = Sulfur dioxide,
TPH = Total Petroleum Hydrocarbons,
SW = surface water
TCR = Total Carcinogenic risk
VOCs = volatile organic compounds
Zn = Zinc
cfu/mL = colony-forming unit per millilitre
ε' = Dielectric constant
μg/kg = micrograms per kilograms
μg/L = micrograms per litre
μs/cm = microsiemens/centimeter

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