Heliyon 9 (2023) e20631

Contents lists available at ScienceDirect

Heliyon

journal homepage: www.cell.com/heliyon

Water quality index, ecotoxicology and human health risk modelling of surface and groundwater along illegal crude oil refining sites in a developing economy

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A R T I C L E I N F O

Keywords:
Crude oil refining
Ecotoxicology
Groundwater
Human health risk
Surface water
Water quality index

A B S T R A C T

Water quality index, ecotoxicology and human health risk models were applied to surface and groundwater samples along illegal crude oil refining sites in Rivers State, Nigeria. Eight (8) surface water and four (4) groundwater sampling points were identified along illegal refining sites. Thirty-six (36) samples in triplicates were collected monthly from each of the twelve (12) sampling points over a three (3) month period. Water samples were collected and analyzed using standard methods as prescribed by the American Public Health Association. The mean pH for surface and groundwater ranged from 5.61 ± 0.15 to 7.34 ± 0.10 and 5.80 ± 0.10 to 6.39 ± 0.13, respectively. Turbidity, TDS, and BOD data for surface water samples exceeded the WHO guideline values. The ionic dominance pattern of anions for both surface and groundwater water samples were the same and in the order $Cl^- > SO_4^{2-} > NO_3^- > PO_4^{2-}$. Mean heavy metal concentration was in the order Pb > Ni > Fe > Cd > Mn > Cu for surface water and Pb > Cd > Fe > Mn > Ni > Cu for groundwater. Cd and Pb concentrations in both sources were generally high, with Cd exceeding the WHO guideline value (GV). The CCME water quality index model ranked 62.5% of surface water as marginal, 12.5% as good, 12.5% as poor, and 12.5% as fair. The impact of heavy metals on public health was in the order Pb > Cd > Ni > Fe > Mn, with 83% of samples seriously affected by Pb pollution. The potential ecological risk index ranged from 1.61×10^3 to 2.64×10^3 for surface water and 8.10×10^2 to 2.21×10^3 for groundwater. Heavy metal contamination was very high, and the ecological risk effect was extremely high. The health risk through oral ingestion was in the order of adults > infants > children. Two principal components, PC1 and PC2, explained 50.51% and 16.00% of the variations in surface water quality, respectively. For groundwater quality data, three principal components explained the observed variations in water quality data, of which 51.39% is attributed to PC1, 26.29% to PC2, and 16.58% to PC3.

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https://doi.org/10.1016/j.heliyon.2023.e20631
Received 8 January 2023; Received in revised form 30 September 2023; Accepted 3 October 2023
Available online 4 October 2023

1. Introduction

Globally, it is estimated that 190 million illnesses and 60,000 annual fatalities are linked to water pollution [1]. Petroleum production is also known to pollute waters, releasing metals and metalloids into aquifers and surface waters. In the case of developing countries, an estimated 80% of all diseases and one-third of deaths are caused by consumption of polluted water containing high concentrations of As, Cd, Hg and Pb [2,3]. These negative impacts of water pollution, human health risks, and ecosystem destruction are further compounded by population growth, urbanization, and industrialization [4]. Consequently, with 30% of the world's population facing water scarcity [5], water pollution is of global concern.

Meanwhile, illegal crude oil refining exacerbates the impact of water pollution by oil contamination. In Nigeria, one of the global oil-rich nations, specifically the Niger Delta, water pollution through illegal crude oil refining activities is ascending [4]. The Niger Delta has the largest wetland in Africa and is among the world's top ten wetlands and marine ecosystems. However, vandalism of oil infrastructures, oil theft, also known as "illegal bunkering," and illegal refining of crude oil [6,7] contribute to the region being ranked among the fifth most severely petroleum-damaged ecosystems in the world [8]. Illegal refining typically involves metal pipes and drums welded together in which crude oil is vaporised, cooled, and condensed in tanks and transported on river channels to points of sale [4]. The open fire is typically applied to heat boilers, and crude oil is tipped into pits in the ground. As the oil burns, oil seepage into the ground also occurs. This illegal refining of crude oil is known to produce 2% kerosene, 2% fuel, 41% diesel, and 55% as waste being discharged indiscriminately into nearby river channels or soils, leading to environmental pollution [6]. While receiving water bodies and groundwater sources have been significantly degraded by illegal oil refining [9–12] destruction to farmlands, mangrove rain forests, fishing grounds and declination of crabs, molluscs, periwinkles, and fish have also been reported [8]. These illegal activities further define the distribution and speciation of heavy metals in water sources and the geochemical environment.

Rivers State in the Niger Delta is a flat plain State with various river channels from where it derived its name "Rivers State." Unfortunately, surface and groundwater sources in Rivers State have not been spared of the consequences of illegal oil refining posing a threat to humans and aquatic life. Sadly, due to the erratic supply of piped water, there is a high dependency on the consumption and usage of surface and groundwater sources by locals in Rivers States [8], thus potentially exposing adults, children, and infants to adverse human health risks. Extreme water pollution in Rivers State due to illegal crude mining has recently raised a severe public outcry. Currently, for some major water sources in Rivers State, there is inadequate empirical evidence on the speciation and distribution of heavy metals in water sources, pollution levels, and potential human health and ecological risks. This study, therefore, aims to observe and present empirical evidence on metal enrichment in polluted water sources in Rivers States, particularly on water sources barely studied. The potential ecological and human health risks were also elucidated.

Water quality indices present a scientific basis to ascertain pollution in water sources and, intuitively, the distribution of metals. The study uses water quality indices to estimate water sources' current pollution and water quality status. Risk models are widely

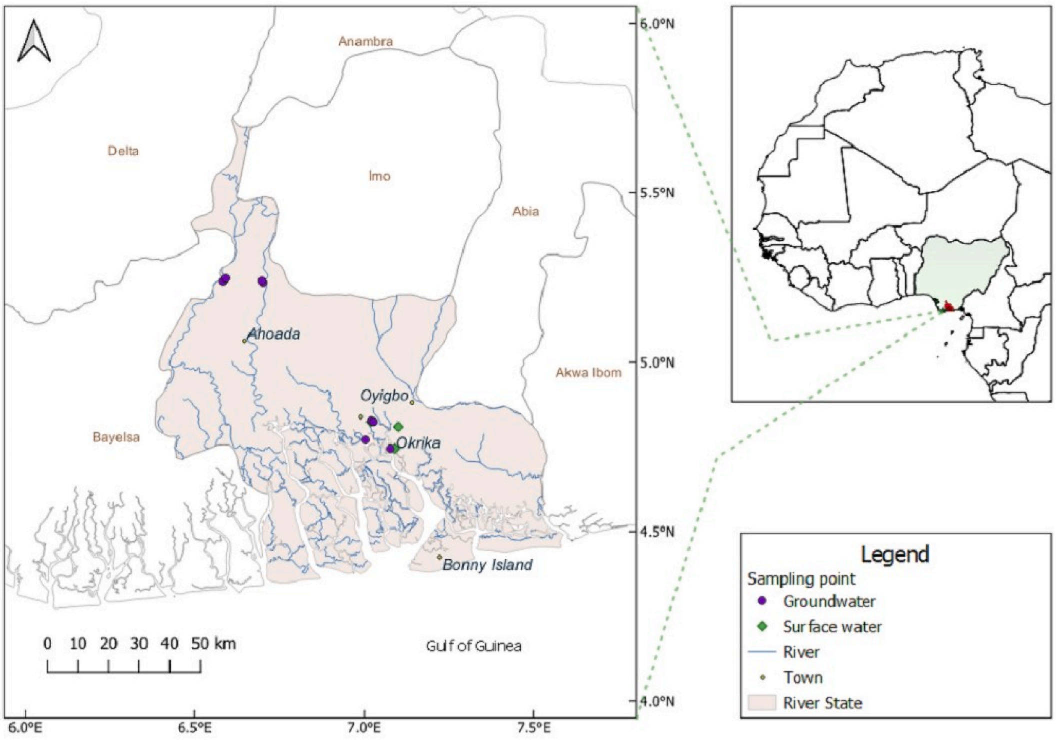


Fig. 1. Map of Rivers State showing sampling location.

applied to establish the potential ecological and human health risks to adults, children, and infants. The scope of this study constitutes a potential early warning sign and empirical evidence to understand the present contamination level and plan management strategy accordingly for public education, development planning, policy, and potential remediation. Furthermore, the study presents valuable insights into the water quality status of some water sources in Rivers State, Nigeria and complements global efforts on water pollution studies. The study is limited to water quality analyses of water sources. It does not include the assessment of bioaccumulation of heavy metals in aquatic species, which is recommended for future studies. The article includes an introduction, materials and methods, results and discussion, and a conclusion.

2. Materials and methods

2.1. Study area

Rivers State is one of the 36 states in Nigeria. It is in the oil-rich area of the Niger Delta. The State is sandwiched in the South by the Atlantic Ocean, to the North by Imo and Abia States, to the East by Akwa-Ibom State and to the West by Bayelsa State and Delta States [13]. The river's flow direction is generally from the northern to the southern region. Eight (8) surface water and four (4) groundwater sampling points were identified along illegal refining sites. In Northern Rivers State, five sampling points were considered consisting of three surface water points, namely Ahoada West River (AWR), Akabta River (AKR) and Idu River (IDR) along the Akabta and Idu communities and two groundwater point sources located in the Akabta and Idu community namely Akabta groundwater (AGW) and Idu groundwater (IGW). Along the Ahoada creeks are sites of illegal oil refining activities. In Southern Rivers State, seven sampling points were considered consisting of five surface water points, namely Okrika Creek (OKC), Okrika Jetty (OKJ), Bakana Creek (BAC), Bakana Jetty (BAJ) and Marine Base River (MBR). Along the Okrika and Bakana creeks are sites of illegal oil refining activities. Two groundwater point sources located in the Marine Base (MGW) and Okrika community (OGW) along Okrika Creek and at the Port Harcourt city centre (CGW) were also sampled. Groundwater samples were collected from the Akabta and Idu communities along the creeks. Thirty-six (36) samples in triplicates were collected monthly from each of the twelve (12) sampling points over a three (3) month period. Fig. 1 represents the map of Rivers State showing sampling points (Boreholes (BH), Surface water (SW) and illegal refining sites (IRS)).

2.2. Sampling, quality control/assurance, and laboratory analyses

Sampling, physicochemical, and bacteriological water quality analyses complied with the standard methods for the examination of water and wastewater [14]. All chemicals used were analytical-grade reagents. For quality assurance and control, samples were collected into sterilized vials and stored in sampling containers for in-situ and ex-situ analyses. With the laboratory analyses, each parameter per sample was analyzed in triplicate and for each experimental run, a blank was included to exclude any batch-specific error. Specifically for metal analyses, sampling vials were acid-cleaned, rinsed with deionized water, and dried for 24 h. Metal analysis samples were acidified in-situ for preservation. It was further ensured that analytical instruments were calibrated appropriately. Blank solutions were also prepared for all spectrophotometric analyses, and fresh solutions were used to prepare calibration curves. For the AAS analyses, reference solutions of each element were used to calibrate the equipment. The calibration curves proved that the instrumentation conditions provided good accuracy and precision.

Physicochemical and bacteriological parameters analyzed include pH, total dissolved solids, turbidity, conductivity, sulphate, nitrate, Biochemical Oxygen Demand, Dissolved Oxygen, and faecal coliforms. Heavy metals analyzed were Iron (Fe), Manganese (Mn), Lead (Pb), Nickel (Ni), Cadmium (Cd), Copper (Cu) and Chromium (Cr).

The pH was determined by immersing a pH meter electrode into the sample until readings were stable. For conductivity, turbidity and total dissolved solids, a glass tube was filled with a sample volume and inserted into the JENWAY 40710, model HI 9032, for readings.

Sulphates, nitrates, and phosphates were determined by filling a glass tube with a sample volume, mixing with powdered reagents, and determining the concentrations using a Hanna Instrument HI 83200 multiparameter spectrophotometer at a predetermined wavelength.

In terms of faecal coliforms, 100 ml of water sample was membrane filtered and placed in a Petri dish containing M − FC agar and incubated for 24 h at a temperature of 36 °C for total coliforms and 44 °C for faecal coliforms.

For heavy metals, 100 ml of water samples were acidified with 20.0 ml HNO_3 solution, and the mixture was heated gently for 20 min to remove any potential interferences. A volume of 5.0 ml of HNO_3 was further added to the solution and heated for an additional 30 min until complete digestion was achieved. The digested sample was left to cool and filtered using Whatman filter paper. Filtrate was analyzed for heavy metals using Atomic Absorption Spectrophotometry. Data from the water quality analyses were used in determining the water quality indices and ecotoxicological and human health risks of the waters under study. The mean values of the parameters analyzed were compared to the WHO guideline values.

2.3. Pollution and health risk assessment

2.3.1. CCME water quality index modelling

The Canadian Council of Ministers of the Environment (CCME) Water Quality Index (WQI) model is a valuable tool for assessing water quality data [15]. The CCME WQI model was applied to water quality data from the study locations. The CCME WQI model consists of three variance measures from selected water quality objectives: Scope, Frequency and Amplitude. Scope "F_1" as represented in Equation (1), determines the extent of water quality guideline non-compliance. Frequency "F_2" in Equation (2), represents the percentage of individual tests that do not meet objectives. Amplitude "F_3" represents the amount by which failed tests do not meet their objectives and it is calculated using Equation (3), (4), (5) and (6). The three factors of scope, frequency and amplitude combine to produce a value between 0 and 100, representing the overall water quality. Each factor is determined by the equations presented:

$$F_1 = \left(\frac{\text{Number of failed variables}}{\text{Total number of variables}}\right) \times 100 \tag{1}$$

$$F_2 = \left(\frac{\text{Number of failed tests}}{\text{Total number of tests}}\right) \times 100 \tag{2}$$

The calculation of amplitude $F_{3,}$ is completed in three steps.

Step 1. Calculation of excursion

Excursion is the number of times an individual concentration is greater than the objective when the objective is maximum or less than the objective, when the objective is minimum.

When the test value must not exceed the objective:

$$\text{Excursion}_i = \left(\frac{\text{Failed Test Value}_i}{\text{Objective}_j}\right) - 1 \tag{3}$$

when the test value must not fall below the objective:

$$\text{Excursion}_i = \left(\frac{\text{Objective}_j}{\text{Failed Test Value}_i}\right) - 1 \tag{4}$$

Step 2. Calculation of normalized sum of excursions

The normalized sum of excursions (nse) determines the extent to which individual tests are out of compliance.

$$\text{nse} = \frac{\sum_i^n \text{excursion}_i}{\text{Number of tests}} \tag{5}$$

Step 3. Calculation of F_3

F_3 is an asymptotic function that scales the normalized sum of excursions from objectives to a range from 0 to 100.

$$F_3 = \left(\frac{\text{nse}}{0.01\text{nse} + 0.01}\right) \tag{6}$$

The CCME WQI is then calculated as shown in Equation (7):

$$\text{CCME WQI} = 100 - \left(\frac{\sqrt{F_1{}^2 + F_2{}^2 + F_3{}^2}}{1.732}\right) \tag{7}$$

The CCME WQI score is then ranked into one of the following five categories:

Excellent: (WQI Value 95–100) - Water quality is protected with a virtual absence of impairment; conditions are very close to natural or pristine levels.

Good: (CWQI Value 80–94) - Water quality is protected with only a minor degree of impairment; conditions rarely depart from desirable levels.

Fair: (WQI Value 65–79) - Water quality is usually protected but occasionally impaired; conditions sometimes depart from desirable levels.

Marginal: (WQI Value 45–64) - Water quality is frequently impaired; conditions often depart from desirable levels.

Poor: (WQI Value 0–44) - Water quality is almost always impaired; conditions usually depart from desirable levels.

2.3.2. *Metal index (MI)*

The metal index (MI) for drinking water accounts for the summative effect of heavy metals on public health. It is a scientific expression as shown in Equation (8) that estimates the overall quality and suitability of drinking water [16].

The MI expression and classification used in this data was as proposed by Ref. [16].

$$MI = \sum \frac{C_i}{(MAC)_i} \tag{8}$$

where MAC = maximum allowable concentration.

C_i = mean concentration of each metal.

Table 1
Mean physicochemical water quality data of surface and groundwater samples.

PARAMETER	Surface water								Groundwater				
	OKC	AWR	BAC	OKJ	MBR	BAJ	AKR	IDR	MGW	AGW	IGW	CGW	WHO
pH	7.27 ± 0.44	6.34 ± 0.21	6.68 ± 0.14	7.34 ± 0.10	7.26 ± 0.13	6.76 ± 0.10	5.61 ± 0.15	5.98 ± 0.09	6.39 ± 0.13	5.97 ± 0.08	5.80 ± 0.10	5.89 ± 0.05	**8.5**
Turb (NTU)	11.9 ± 1.57	16.8 ± 1.31	6.1 ± 0.91	2.9 ± 0.46	4.2 ± 0.78	6.3 ± 0.35	0.8 ± 0.10	2.4 ± 0.61	0.2 ± 0.00	0.2 ± 0.10	0.2 ± 0.00	0.1 ± 0.00	**5**
EC (μS/cm)	3.09E+04 ±8.9E+02	3.29E+04 ±1.08E+03	3.45E+04 ±1.87E+03	2.81E+04 ±1.15E+03	2.40E+04 ±1.44E+03	2.65E+04 ±1.57E+03	24 ± 2.65	34 ± 1.73	26 ± 2.65	75 ± 9.85	335 ± 8.89	51 ± 3.12	**1500**
TDS (mg/L)	2.16E+04 ±9.62E+02	2.26E+04 ±1.05E+02	2.42E+04 ±8.39E+02	1.97E+04 ±8.44E+02	1.68E+04 ±9.53E+02	1.76E+04 ±9.64E+02	17 ± 3.21	23 ± 3.21	18 ± 2.31	53 ± 3.79	234 ± 1.53	35 ± 1.53	**2000**
BOD_5 (mg/L)	37.7 ± 1.37	22.8 ± 1.42	75.4 ± 2.16	14.8 ± 1.76	12.6 ± 1.53	11.4 ± 1.00	1.6 ± 0.15	0.6 ± 0.21	0.37 ± 0.04	0.24 ± 0.02	0.26 ± 0.01	1.6 ± 0.12	**4**
DO (mg/L)	6.77 ± 0.32	6.43 ± 0.13	5.48 ± 0.11	3.96 ± 0.09	2.33 ± 0.11	2.14 ± 0.09	3.69 ± 0.06	3.46 ± 0.10	4.43 ± 0.11	5.84 ± 0.15	5.73 ± 0.05	5.14 ± 0.02	**10**
Salinity ($^0/_{00}$)	19.4 ± 1.17	18.3 ± 1.06	21.8 ± 0.40	17.4 ± 0.68	14.6 ± 1.57	15.6 ± 0.98	0.01 ± 0.00	0.02 ± 0.01	0.01 ± 0.00	0.04 ± 0.01	0.16 ± 0.02	0.03 ± 0.01	**200**
TH (mg/L $CaCO_3$)	19.4 ± 1.32	15.4 ± 0.71	3360 ± 210.71	7200.0 ± 1058.3	6960.0 ± 144.2	5400.0 ± 264.6	7.70 ± 0.95	11.52 ± 1.13	17.30 ± 0.95	7.70 ± 0.56	36.53 ± 1.85	12.50 ± 0.96	**150**
Alk (mg/L $CaCO_3$)	40 ± 3.06	32 ± 2.65	84 ± 3.61	42 ± 3.61	54 ± 3.06	6 ± 2.57	4 ± 1.00	63 ± 2.65	5 ± 2.57	4 ± 1.00	42 ± 2.65	5 ± 0.50	**-**
Cl^- (mg/L)	5.0E+03 ± 115.13	4.9E+03 ± 102.87	1.2E+04 ± 185.55	4.6E+03 ± 74.94	4.3E+03 ± 138.9	4.3E+03 ± 174.8	0.58 ± 0.31	1.00 ± 0.26	1.50 ± 0.26	5.20 ± 0.36	1.03 ± 0.21	3.35 ± 0.23	**250**
SO_4^{2-} (mg/L)	1.1E+03 ± 93.04	1.2E+03 ± 61.22	1.0E+03 ± 77.59	1.0E+03 ± 59.35	957.0 ± 63	988.0 ± 27.62	0.66 ± 0.20	0.58 ± 0.31	3.30 ± 0.46	0.45 ± 0.21	2.60 ± 0.58	2.15 ± 0.34	**200**
NO_3^- (mg/L)	0.24 ± 0.04	0.22 ± 0.04	0.31 ± 0.03	0.23 ± 0.02	0.22 ± 0.03	0.29 ± 0.03	0.26 ± 0.02	0.61 ± 0.06	0.38 ± 0.01	0.46 ± 0.01	2.96 ± 0.02	0.42 ± 0.01	**50**
PO_4^{3-} (mg/L)	0.13 ± 0.02	0.14 ± 0.02	0.11 ± 0.03	0.19 ± 0.02	0.29 ± 0.05	0.21 ± 0.04	0.01 ± 0.01	0.05 ± 0.01	0.08 ± 0.01	0.07 ± 0.01	0.11 ± 0.01	0.08 ± 0.01	**0.5**
Mn (mg/L)	0.067 ± 0.003	0.006 ± 0.001	0.039 ± 0.002	0.072 ± 0.003	0.092 ± 0.001	0.034 ± 0.003	0.036 ± 0.002	0.033 ± 0.002	0.046 ± 0.001	0.032 ± 0.001	0.004 ± 0.00	0.051 ± 0.001	**0.1**
Fe (mg/L)	0.407 ± 0.004	2.536 ± 0.005	0.285 ± 0.003	0.354 ± 0.005	0.413 ± 0.005	0.313 ± 0.006	0.159 ± 0.005	1.160 ± 0.029	0.082 ± 0.000	0.049 ± 0.001	0.076 ± 0.001	0.007 ± 0.0	**0.3**
Cd (mg/L)	0.172 ± 0.009	0.159 ± 0.005	0.151 ± 0.005	0.172 ± 0.005	0.171 ± 0.003	0.154 ± 0.004	0.178 ± 0.003	0.188 ± 0.003	0.178 ± 0.001	0.204 ± 0.000	0.183 ± 0.001	0.154 ± 0.0	**0.003**
Cu (mg/L)	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	**0.5–2.0**
Ni (mg/L)	0.229 ± 0.013	0.09 ± 0.000	0.175 ± 0.009	0.201 ± 0.006	0.211 ± 0.006	0.175 ± 0.005	0.053 ± 0.011	0.294 ± 0.010	0.002 ± 0.001	0.063 ± 0.000	0.001 ± 0.001	0.002 ± 0.0	**0.02**
Pb (mg/L)	1.729 ± 0.047	0.002 ± 0.001	1.145 ± 0.008	0.802 ± 0.009	0.764 ± 0.011	0.832 ± 0.005	0.002 ± 0.001	0.301 ± 0.007	0.203 ± 0.002	0.301 ± 0.000	0.179 ± 0.001	0.178 ± 0.0	**0.01**
HBC (cfu/100 ml)	120.0 ± 15.10	67.0 ± 4.58	75.0 ± 3.00	185.0 ± 2.65	210.3 ± 7.23	176.0 ± 3.61	105.0 ± 1.00	56.3 ± 2.08	82.3 ± 1.53	40.0 ± 1.00	4.1 ± 0.12	61.0 ± 1.00	**Nil**

Ahoada West River (AWR), Akabta River (AKR) and Idu River (IDR), Okrika Creek (OKC), Okrika Jetty (OKJ), Bakana creek (BAC), Bakana Jetty (BAJ), Marine Base River (MBR), Marine Base (MGW) and Okrika community (OGW), City centre groundwater (CGW).

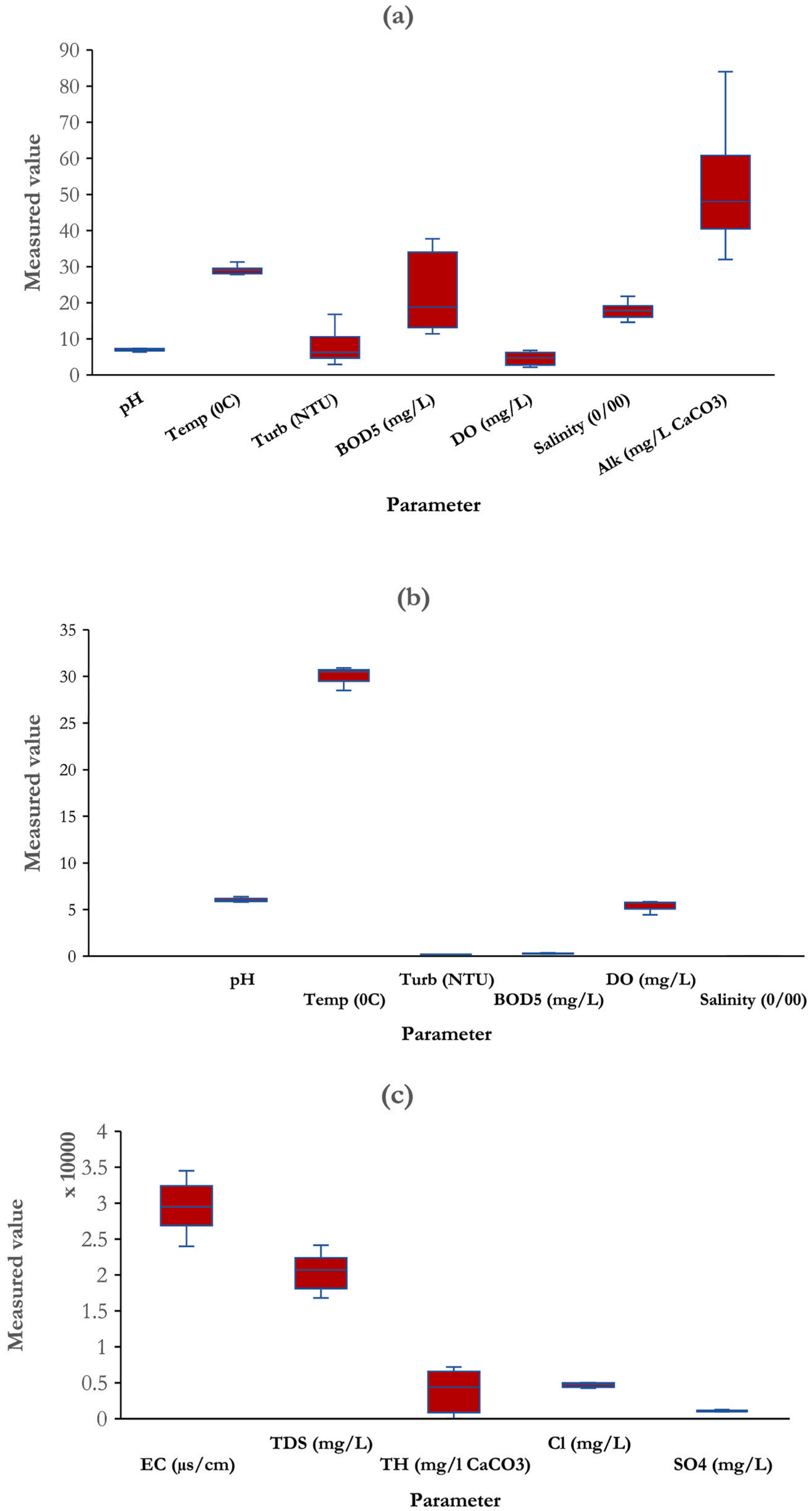
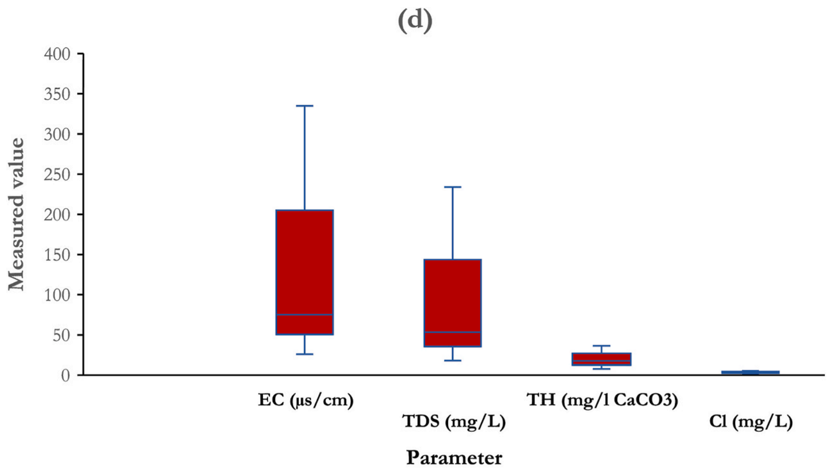
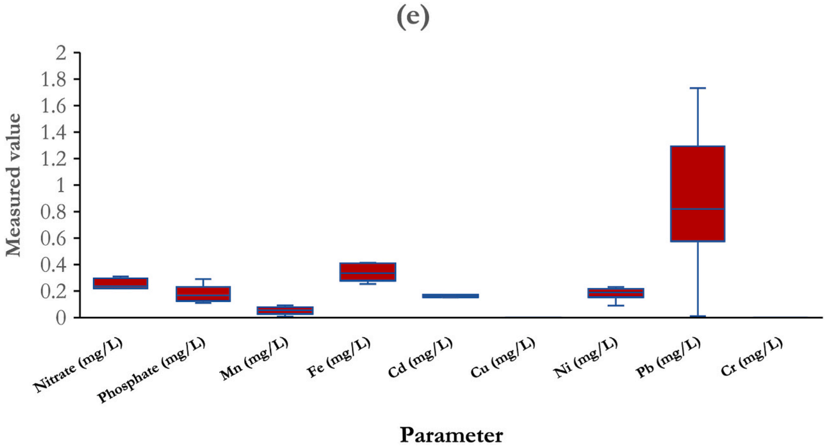


Fig. 2. Box plot of physicochemical parameters for surface water (a, c, e) and groundwater (b, d, f).





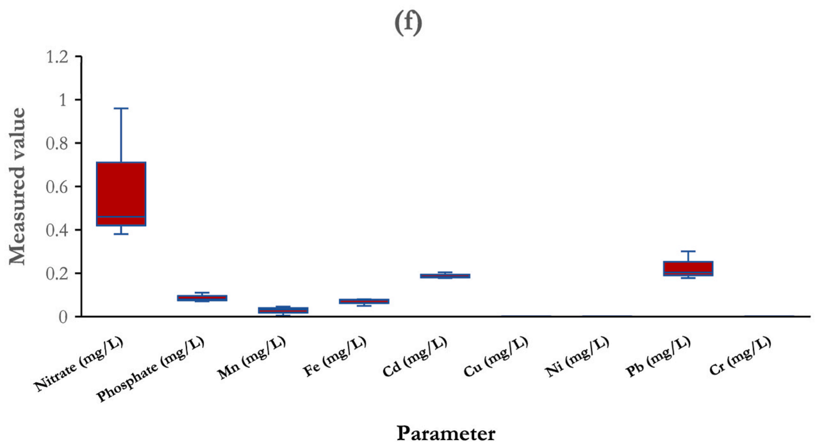


Fig. 2. (*continued*).

2.3.3. Potential ecological risk index (PERI)

The Potential Ecological Risk Index (PERI) method as proposed by Hakanson assesses the behaviour of heavy metal contaminants [16]. The Hakanson method assesses the potential ecological and environmental effects of metals computed from the contamination coefficient, the toxic response factor for heavy metals, a comprehensive contamination measure. The potential ecological risk is calculated as follows using Equations (9)–(11):

$$E_r = T_i \times C_f \tag{9}$$

$$C_f = \frac{C_i}{S_i} \tag{10}$$

$$PERI = \sum E_r \tag{11}$$

where C_f = Contamination factor.

S_i = Reference value of metal.

T_i = Toxic response factor.

The T_f for Mn, Cd, Ni and Pb as suggested by Hakanson are 1, 30, 5, and 5, respectively [16]. The degrees of contamination and the potential ecological risk evaluation standards were adopted from relevant literature [17,18] and presented in Table A3.

2.3.4. Human health risk (HHR) modelling

The potential human health risk (HHR) assessment evaluates water's possible adverse harmful human health impact on infants, children, and adults [16]. Ingesting pathways could be oral or dermal. This study adopted the oral ingestion pathway because the HHR assessment through the dermal way has been reported to be relatively uncertain [19]. The HHR was determined using Equations (12) and (13) [20,21] to measure the exposure dose (E) through ingestion pathway and potential non-carcinogenic risk of Hazard Quotient (HQ):

$$E = \frac{CPW \times IR \times ED \times EF}{ABW \times AET} \tag{12}$$

$$HQ = \frac{E}{RfD} \tag{13}$$

where E is the chronic daily intake (mg/kg/day), CPW is the concentration of a particular contaminant in surface or groundwater (mg/L), IR is the human ingestion rate (L/day: 2.5 L/day for adults, 0.78 L/day for children, and 0.3 L/day for infants [22]. ED is the exposure duration (64, 12, and <1 year for adults, children, and infants, respectively), EF is the exposure frequency (365 days for adults, children, and infants), ABW is the average body weight (57.5 Kg, 18.7 Kg, and 6.9 Kg for adults, children, and infants, respectively), AET is the average time (23360, 4380, and 365 days for adults, children, and infants, respectively), HQ is the non-carcinogenic for hazard quotient, RfD is the reference dose. HQ values < 1 indicate no obvious non-carcinogenic risk or acceptable level, and >1 indicate an unacceptable risk of adverse non-carcinogenic effects on health [22].

2.4. Statistical analyses

Descriptive statistics, including means, standard deviations, and ranges, were analyzed using MS Excel. Univariate and multivariate analyses for the test of significance, ANOVA and principal component analysis were performed using Statistical Package for Social Sciences (SPSS) version 22. PCA is a dimension reduction statistical inference widely adopted to explain observed variances of inter-correlated independent variables [23–26].

3. Results and discussion

3.1. Surface and groundwater quality

Physicochemical and bacteriological parameters were analyzed for both surface and groundwater. A summary of water quality parameters analyzed is presented in Table 1. Box plots of mean values of physicochemical parameters for surface and groundwater samples are presented in Fig. 2 a, c, e for surface water and b, d, f for groundwater.

3.1.1. Hydrogen ion concentration (pH)

The pH of drinking water measures its acidity or alkalinity. However, the WHO establishes no health-based guideline value, and many operational, biological, and catalytic processes are pH dependent. The WHO recommends a range of 6.5–8.5 for drinking purposes. Mean values of pH for surface water ranged from 5.61 ± 0.15 to 7.34 ± 0.10, with a mean of 6.94 ± 0.4. pH at Akabta River, Idu River and Bakana Creek were slightly acidic and exceeded the WHO guideline value. pH of groundwater samples ranged from 5.80 $\pm$ 0.10 to 6.39 ± 0.13. All groundwater samples were somewhat acidic and exceeded the WHO guideline value. Acidic water, when consumed, may contribute to acidosis, a condition where the body fluids become too acidic, causing hyperventilation, impaired heart function and low blood pressure [27]. Acidic waters may cause dental erosion and teeth demineralization [27]. pH also determines the survival of aquatic life and biological activity. Microorganisms usually produce acidic or basic metabolic waste to support microbial activities, thus influencing water pH [28]. The pH of Bodo Creek in the Niger Delta fluctuates between mild acidic and alkalinity [29]. Like the present study, others also recorded pH values ranging from 5.27 to 6.56 in the Niger Delta region [30].

3.1.2. Turbidity

Turbidity is a measure of the cloudiness of water caused by suspended particles, precipitates of metals or organic substances [31]. High turbid water raises concerns about possible contamination, pollution, and water safety. The turbidity of measured surface water samples ranged from 2.9 ± 0.46 NTU to 16.8 ± 1.31 NTU, exceeding the WHO GV. However, turbidity for surface waters at control points was observed as 0.8 ± 0.10 to 2.4 ± 0.61 NTU within the WHO GV. All groundwater samples were also within the WHO GV. Turbidity values ranging from 1.0 to 19.0 NTU in the Azuabie Creek in the Niger Delta region, comparable to data obtained in the present study, have been reported [32,33]. The occurrence of oil spillage, carbon depositions, organic compounds, and suspended particles, all common during illegal oil refining, may have contributed to the observed turbidity [34]. High turbidity interferes with water disinfection and provide sites for attachment for bacterial growth and biofilm formation.

3.1.3. Electric conductivity

Electric conductivity (EC) measures ionic concentrations of water sources induced by dissolved minerals [31]. The observed EC data of surface waters at crude oil refining sites greatly exceeded the WHO guideline value of 1000 μS/cm. Pits and trenches dug for illegal crude oil refining increase soil-water interactions. This facilitates the release of inorganic ions into water and increases the EC. However, the surface water samples at control points and groundwater samples were within the WHO GV. The disparity in EC data between the surface water samples at the illegal sites and control points establishes the impact of active cottage activities and illegal crude oil refining, potentially imparting dissolved salts, and minerals to the surface water, thereby increasing the EC.

3.1.4. Total dissolved solids (TDS)

Total Dissolved Solids (TDS) indicate water's palatability due to inorganic salts and minerals [31,35,36]. TDS less than 600 mg/L is considered good, but greater than 1000 mg/L renders water unpalatable [31]. Surface water sampling points at illegal crude oil refining sites recorded very high TDS values. TDS ranged from 1.68×10^4 to 2.42×10^4 mg/L, exceeding the WHO GV and deviating from freshwater. Bakana Creek recorded the ′highest total dissolved solids with a mean value of 2.42×10^4 mg/L. Observed data for surface waters at Akabta River ranged from 17 to 23 mg/L within the WHO GV. Data for groundwater samples for TDS ranged from 18 to 234 mg/L within the WHO GV. TDS values for surface waters at control points and groundwater samples were of freshwater type [34]. However, saline water was TDS for surface waters at illegal oil refining sites. A positive correlation between measured TDS values recorded at the illicit refining sites and EC values was observed. This reflects that increased anthropogenic activities due to illegal refining increase TDS in water, which induces EC as dissolved minerals are ionised in water.

3.1.5. Biochemical Oxygen Demand (BOD)

Biochemical Oxygen Demand (BOD) measures the oxygen microorganisms need to degrade organic matter. BOD Data for surface water samples exceeded the WHO guideline value for BOD. Bakana Creek recorded the highest mean BOD value of 75.40 ± 2.16 mg/L. The Idu River recorded the least BOD value of 0.60 ± 0.21 mg/L. BOD data for groundwater samples ranged from 0.37 ± 0.04 to 1.6 ± 0.12 mg/L within the WHO GV. High BOD values can be inferred from the potential oil spillage during illegal crude oil refining and transporting. Crude oil is rich in hydrocarbons, and when split into water, it increases the organic constituent, implicitly increasing the BOD. Water quality data showed that apart from the Akabta and Idu rivers, all other surface water points were not within the WHO guideline value of 4.0 mg/L.

3.1.6. Dissolved oxygen (DO)

Dissolved Oxygen (DO) maintains the freshness of water. Low dissolved oxygen in water can stimulate anaerobic denitrification of nitrate to nitrite. No health-based guideline value is established by the WHO. The highest concentration of DO was 6.77 ± 0.32 mg/L recorded at Okrika Creek, and the lowest value of 2.14 ± 0.09 mg/L was recorded at the Bakana Jetty. DO concentrations of 6.07, 5.75 and 5.38 for Okpare, Okrika and Nembe, all within the Niger Delta region have been reported in other studies [37]. Field observation revealed the visual presence of oil and grease film on the surface water body due to illegal crude oil refining activities. Oil and grease films inhibit the dissolution of atmospheric oxygen into the water, reducing the freshness and quality [30,38].

3.1.7. Major anions

The ionic dominance pattern for anions for all water samples was in the order of chlorides > sulphates > nitrates > phosphates.

Chloride can taste salty to water, mainly when sodium is the predominant cation. Excess chloride in water is generally an indication of pollution [14]. Mean chloride values recorded at Okrika Creek, Ahoada west river, Bakana Creek, Okrika Jetty, and Marine base river far exceeded the WHO recommended guideline values of 250 mg/L by several thousand mg/L. Data for chloride at Akabta, Idu River and groundwater samples were within the WHO GV. Chlorides are non-cumulative toxins, and only an excess amount ingested over time may constitute a health hazard [39].

Sulphates are usually found in naturally occurring minerals. High concentrations in surface water may be an indication of industrial wastewater discharge. Gastrointestinal effects have been associated with ingesting water with high sulphate concentrations [40]. Ahoada west river recorded the maximum amount of $1.2 \times 10^3 \pm 61.22$ mg/L sulphate concentration, and Marine base river recorded the least concentration of $9.6 \times 10^2 \pm 63.00$ mg/L. Measured values far exceeded the WHO recommended guideline values of 200 mg/L. Trace concentrations of ≤1.00 mg/L sulphate were detected at the Akabta and Idu rivers. Sulphate concentrations across sample locations were statistically significant at $p < 0.05$. The significant variations in the observed sulphate concentrations reflect the impact of natural or anthropogenic occurrences, such as illegal mining, on the sulphate concentration at each sampling location. Data for groundwater samples were within the WHO allowable limit for sulphate. High sulphate values ranging from 1.815 mg/L to 3197 mg/L were also reported at Elechi Creek in the Niger Delta [41]. High sulphate concentrations could be attributed to leachates from dumpsites and industrial effluents discharged into the surface water body.

Nitrate is naturally occurring and remains one of the widespread contamination sources to surface and groundwater [42–44]. Using or overusing fertilizers for agriculture can elevate nitrate concentrations in water through run-off. Ingestion of high nitrate concentrations is known to cause blue-baby syndrome in children. Nitrate concentration for surface water and groundwater samples ranged from 0.22 to 0.61 mg/L and 0.38–2.96 mg/l, respectively. Idu River recorded the highest nitrate concentration of 0.61 ± 0.06 mg/L, and Marine base river recorded the least concentration of 0.22 ± 0.03 mg/L. All surface water and groundwater samples analyzed for nitrates were within WHO GV of 50 mg/L. The relatively high concentration observed at the Idu River indicates possible contamination from anthropogenic activities such as fertilizer application from farming, cottage industrial effluents, animal wastes, domestic effluents, and leakages from septic tanks. Mean nitrate concentrations ranging from 0.12 mg/L to 2.08 mg/L at the Nun River estuary in the Niger Delta region has been observed [30]. Mean nitrate values of 0.117–0.394 mg/L [41] and 0.71–1.82 mg/L [45] in surface waters in Niger Delta have been reported.

Mean phosphate values for both surface and groundwater were within the WHO recommended GV. Both Surface and groundwater also recorded high loads of microbial contamination.

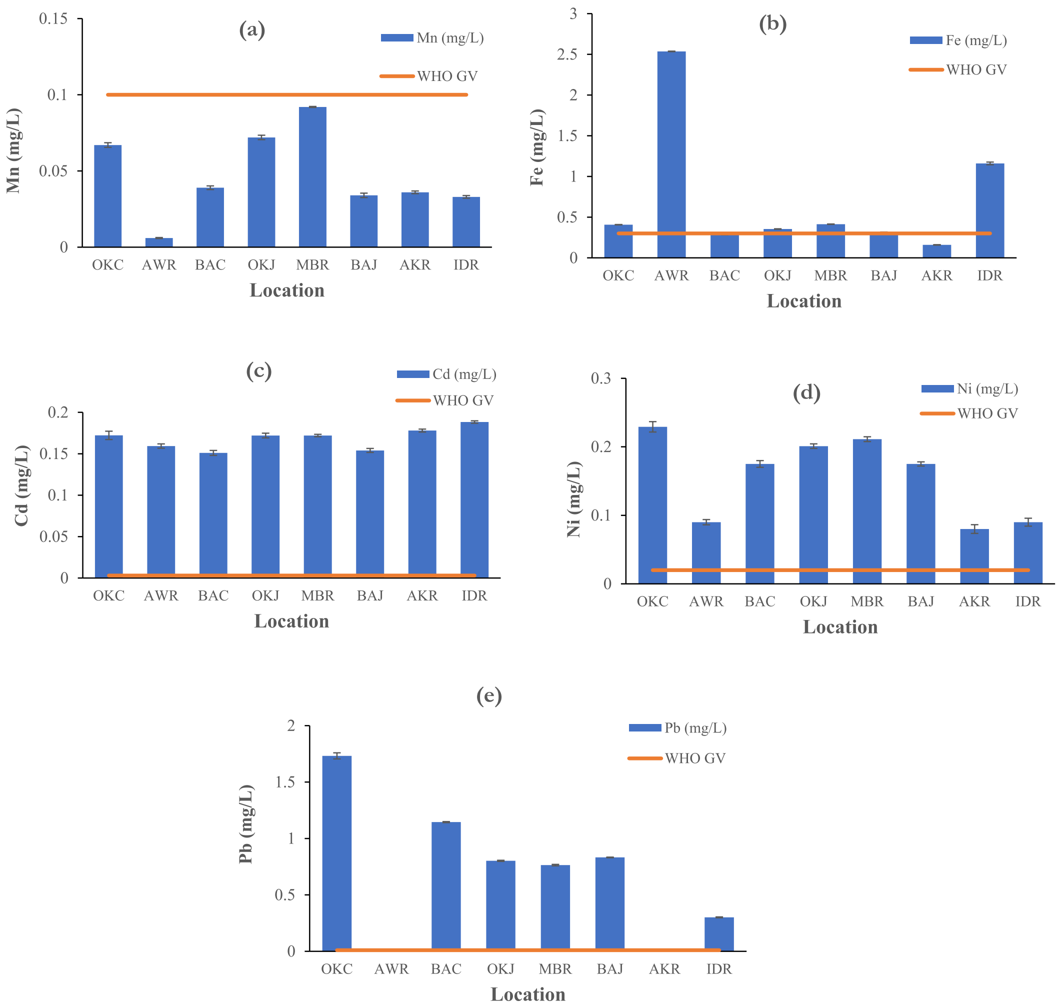


Fig. 3. Mean concentration of heavy metals for surface water sources at sampling points for (a) Mn (b) Fe (c) Cd (d) Ni and (e) Pb.

3.2. Heavy metals

Table 1 presents a summary of mean concentrations of heavy metals. For all surface water samples, mean heavy metal concentrations were in the order Pb > Ni > Fe > Cd > Mn > Cu. For groundwater samples, mean heavy metals were in the order Pb > Cd > Fe > Mn > Ni > Cu. In general, concentrations of Cu were below detectable limits. Concentrations of Mn for surface and groundwater samples were within the WHO GV for drinking water.

3.2.1. Iron (Fe)

Iron has been associated with genetic and metabolic diseases [3]. Although quantities of drinking water are usually low, they present aesthetic and acceptability challenges to consumers. From the study, the highest Iron concentration of 2.536 ± 0.80 mg/L was observed at Ahoada West illegal refining site, and Akabta River recorded the least concentration of 0.159 ± 0.02 mg/L. The iron concentrations were above the WHO GV of 0.3 mg/L except for Bakana and Akabta rivers. Iron concentrations for groundwater samples were all within the WHO-acceptable GV. Soil-water interactions tend to increase Fe concentration in water. Additionally, rust from iron tanks, make-shift structures and mechanical equipment at illegal oil refining sites could be a potential source of iron to surface water.

3.2.2. Cadmium (Cd)

Cadmium is known to cause renal injuries, immune deficiencies, bone injuries, femoral pain, and skeleton deformations [46]. Cd is also known to hinder plants' photosynthesis activity [39]. Exposure to high concentration of Cd can lead to cardiovascular pathologies, including haemorrhagic injury, atherosclerosis, hypertension, and cardiomyopathy [47]. From the study, mean Cd concentrations recorded for surface water at sampling sites ranged between 0.151 and 0.188 mg/L, and groundwater samples ranged from 0.154 to 0.204 mg/L. Cd concentrations for water samples exceeded the acceptable WHO GV. Cadmium concentrations of 0.004 mg/L were recorded by Ref. [48] in Delta State. Both surface and groundwater samples analyzed were heavily polluted with Cd, with mean concentrations exceeding the WHO guideline value of 0.003 mg/L. The Cd concentrations reported are a health concern as high concentrations of Cd can cause poisoning if ingested. The engagement also reflects the impact of illegal mining on water resources. Cadmium concentrations recorded at surface water sampling locations significantly differed with $p < 0.05$. Similar Cd concentrations were observed by Ref. [49].

3.2.3. Lead (Pb)

Lead is associated with poor intellectual ability and development in children [3]. Health complications like early membrane rupture, spontaneous abortion, erectile dysfunction, cardiovascular diseases, and negative pregnancy outcomes are also associated with Pb [3]. All the water samples recorded Pb concentrations higher than the WHO guideline of 0.05 mg/L except the Ahoada West River and the Akabta River, which recorded concentrations of less than 0.01 mg/L. Pb concentrations across the various locations were statistically significant, $p < 0.05$. The occurrence of Pb in the samples could be attributed to leaching from batteries and other dry cells used onsite. Similar Pb concentrations ranging from 0.01 mg/L to 0.61 mg/L for a mangrove creek [50], 0.006 mg/L along the Imonite Creek [51] and 0.001 mg/L to 0.008 mg/L on five rivers [48] in the Niger Delta have also been reported. Low concentrations recorded by other authors could be attributed to fallow periods with reduced illegal crude oil refining due to law enforcement. Fig. 3 shows heavy metal concentrations for surface water samples.

3.2.4. Nickel (Ni)

Nickel (Ni) is a well-recognized carcinogen and a common sensitizing agent with a high prevalence of allergic contact dermatitis [52]. Both surface and groundwater samples were heavily polluted with Ni. Mean concentrations for groundwater samples ranged from 0.001 ± 0.001 to 0.063 ± 0.000 mg/L, and that of surface water samples were from 0.09 ± 0.000 to 0.229 ± 0.013 mg/L. Ni concentrations for all surface water samples exceeded the WHO guideline value for drinking water. Okrika Creek recorded the highest concentration of Ni. The concentrations recorded present adverse health risks to consumers.

Table 2
CCME WQI ranking.

Sampling point	Scope (F1)	Frequency (F2)	Excursion	Normalized sum of errors (NSE)	Amplitude (F3)	CCME WQI ranking	Effect
OKC	55.56	52.63	89.42	1.57	1.54	55.81	Marginal
AWR	50.00	47.37	156.62	2.75	2.67	60.20	Marginal
BAK	61.11	57.89	309.56	5.43	5.15	51.31	Marginal
OKJ	61.11	57.89	237.12	4.16	3.99	51.34	Marginal
MBR	61.11	57.89	273.43	4.80	4.58	51.33	Marginal
BAJ	72.22	68.42	296.49	5.20	4.94	42.49	Poor
AKR	16.67	15.79	60.93	1.07	1.06	86.73	Good
IDR	27.78	26.32	96.80	1.70	1.67	77.89	Fair
MGW	11.11	10.53	77.63	1.36	1.34	91.13	Good
AGW	11.11	10.53	96.10	1.69	1.66	91.11	Good
IGW	11.11	10.53	76.80	1.35	1.33	91.13	Good
CGW	16.67	15.79	71.23	1.25	1.23	86.73	Good

Table 3
Ecological risk index.

	Heavy metal							
Location	Mn	Cd	Ni	Pb	∑Cf	Cf effect	Ecological Risk Index = ∑PERI	Ecological risk effect
OKC/mg/L	0.067	0.172	0.229	1.729	242.35	Very high	2.64E+03	Extremely high
Contamination factor (cf)	0.67	57.33	11.45	172.90				
Cf effect	Non-contamination	Heavy	Heavy	Heavy				
Potential ecological risk	Low	Very strong	Low	Very strong				
AWR/mg/L	0.006	0.159	0.069	0.002	56.62	Very high	1.61E+03	Extremely high
Contamination factor (cf)	0.06	52.89	3.43	0.23				
Cf effect	Non-contamination	Heavy	Heavy	Non-contamination				
Potential ecological risk	Low	Very strong	Low	Low				
BAC/mg/L	0.039	0.151	0.175	1.145	173.96	Very high	2.13E+03	Extremely high
Contamination factor (cf)	0.39	50.33	8.73	114.50				
Cf effect	Non-contamination	Heavy	Heavy	Heavy				
Potential ecological risk	Low	Very strong	Low	Strong				
OKJ/mg/L	0.072	0.172	0.201	0.802	148.47	Very high	2.18E+03	Extremely high
Contamination factor (cf)	0.07	0.17	0.20	0.80				
Cf effect	Non-contamination	Heavy	Heavy	Heavy				
Potential ecological risk	Non-contamination	Heavy	Heavy	Heavy				
MBR/mg/L	0.092	0.171	0.211	0.764	146.36	Very high	2.15E+03	Extremely high
Contamination factor (cf)	0.92	57.11	10.55	76.40				
Cf effect	Non-contamination	Heavy	Heavy	Heavy				
Potential ecological risk	Low	Very strong	Low	Strong				
BAJ/mg/L	0.034	0.154	0.175	0.832	144.78	Very high	2.00E+03	Extremely high
Contamination factor (cf)	0.34	51.44	8.75	83.20				
Cf effect	Non-contamination	Heavy	Heavy	Heavy				
Potential ecological risk	Low	Very strong	Low	Strong				
AR/mg/L	0.036	0.178	0.053	0.002	63.20	Very high	1.80E+03	Extremely high
Contamination factor (cf)	0.36	59.44	2.67	0.20				
Cf effect	Non-contamination	Heavy	Moderate	Non-contamination				
Potential ecological risk	Low	Very strong	Low	Low				
IR/mg/L	0.033	0.188	0.066	0.301	111.83	Very high	2.05E+03	Extremely high
Contamination factor (cf)	0.33	62.78	3.32	30.13				
Cf effect	Non-contamination	Heavy	Heavy	Heavy				
Potential ecological risk	Low	Very strong	Low	Moderate				

(*continued on next page*)

Table 3 (*continued*)

	Heavy metal							
Location	Mn	Cd	Ni	Pb	∑Cf	Cf effect	Ecological Risk Index = ∑PERI	Ecological risk effect
AGW/mg/L	0.046	0.178	0.002	0.203	80.10	Very high	1.88E+03	Extremely high
Contamination factor (cf)	0.46	59.22	0.12	20.3				
Cf effect	Non-contamination	Heavy	Non-contamination	Heavy				
Potential ecological risk	Low	Very strong	Low	Low				
IGW/mg/L	0.032	0.204	0.063	0.301	101.57	Very high	2.21E+03	Extremely high
Contamination factor (cf)	0.32	68.00	3.15	30.10				
Cf effect	Non-contamination	Heavy	Heavy	Heavy				
Potential ecological risk	Low	Very strong	Low	Moderate				
MGW/mg/L	0.004	0.076	0.183	0.001	34.78	Very high	8.10E+02	Extremely high
Contamination factor (cf)	0.04	25.44	9.17	0.13				
Cf effect	Low	Low	Low	Low				
Potential ecological risk	Low	Very strong	Low	Low				
CGW/mg/L	0.051	0.007	0.154	0.002	79.08	Very high	1.92E+03	Extremely high
Contamination factor (cf)	0.04	61.11	0.07	17.87				
Cf effect	Low	Low	Low	Low				
Potential ecological risk	Low	Very strong	Low	Low				
WHO GV	0.100	0.003	0.020	0.01				

Ahoada West River (AWR), Akabta River (AKR) and Idu River (IDR), Okrika Creek (OKC), Okrika Jetty (OKJ), Bakana creek (BAC), Bakana Jetty (BAJ), Marine Base River (MBR), Marine Base (MGW) and Okrika community (OGW), City centre groundwater (CGW).

3.3. CCME WQI model

The CCME WQI model was applied to surface and groundwater quality data to assess its acceptability. The physicochemical properties of the waters were used to assess the purity level according to Equation (7). The computed value of the WQI for surface water samples ranged from 42.49 to 86.73, with an average of 59.64. WQI for groundwater samples ranged from 86.73 to 91.13, with an average of 90.03. According to the CCME WQI model, 62.5% of the surface water analyzed was marginal, implying that water quality is frequently threatened or impaired and conditions often depart from natural or desirable levels; 12.5% were good, indicating water quality is protected with only minor degree of threat or impairment, conditions rarely depart from natural or desirable levels; 12.5% were poor, implying water quality is almost always threatened or impaired, conditions usually depart from natural or desirable levels; and another 12.5% fair, which meant that water quality is generally protected but occasionally threatened or impaired and conditions sometimes depart from natural or desirable levels. All groundwater samples were ranked as good. The calculated CCME WQI values establish the impact of illegal mining on surface water quality. The CCME WQI ranking is presented in Table 2.

3.4. Pollution and metal indices

The Pollution Index (PI) for surface water, presented in Table A1 was found to be 125.772, which was greater than the critical threshold of 100. The Metal index (MI) for surface water, as depicted in Table A2 provides a summative effect of the probable impact of heavy metals on public health. It presents a quicker assessment of the quality of a drinking water source. The metal index ranged from 0.52 to 88.09. The MI based on average values is shown in Table A4. The impact of each metal on public health was in the order Pb > Cd > Ni > Fe > Mn. All metals except for Mn exceeded the threshold of warning. Cumulatively, the MI exceeded the critical threshold value raising public health concerns. The impact of each metal on public health at each sampling location is presented in Table A4. For sampling locations, MI ranged from 63.20 to 243.71. From the MI data, 25% and 75% of groundwater and surface water samples, respectively, raise public health concerns.

Table 4
Calculated health risk for adults, children, and infants at sampling locations.

Mn				
Sample location	Adults	Children	Infants	Health risk
OKC	2.08E-02	2.00E-02	2.06E-02	No obvious non-carcinogenic adverse health risk for [a]ACI
AWR	1.86E-03	1.79E-03	1.84E-03	No obvious non-carcinogenic adverse health risk for ACI
BAK	1.21E-02	1.16E-02	1.20E-02	No obvious non-carcinogenic adverse health risk for ACI
OKJ	2.24E-02	2.15E-02	2.21E-02	No obvious non-carcinogenic adverse health risk for ACI
MBR	2.86E-02	2.74E-02	2.83E-02	No obvious non-carcinogenic adverse health risk for ACI
BAJ	1.06E-02	1.01E-02	1.05E-02	No obvious non-carcinogenic adverse health risk for ACI
AKR	1.12E-02	1.07E-02	1.11E-02	No obvious non-carcinogenic adverse health risk for ACI
IDR	1.02E-02	9.83E-03	1.01E-02	No obvious non-carcinogenic adverse health risk for ACI
MGW	1.43E-02	1.37E-02	1.41E-02	No obvious non-carcinogenic adverse health risk for ACI
AGW	9.94E-03	9.53E-03	9.84E-03	No obvious non-carcinogenic adverse health risk for ACI
IGW	1.24E-03	1.19E-03	1.23E-03	No obvious non-carcinogenic adverse health risk for ACI
CGW	1.58E-01	1.52E-01	1.57E-01	No obvious non-carcinogenic adverse health risk for ACI
Cd				
Sample location	Adults	Children	Infants	Health risk
OKC	1.50E+01	1.44E+01	1.48E+01	Unacceptable risk of adverse non-carcinogenic health effects for ACI
AWR	1.39E+01	1.33E+01	1.37E+01	Unacceptable risk of adverse non-carcinogenic health effects for ACI
BAK	1.31E+01	1.26E+01	1.30E+01	Unacceptable risk of adverse non-carcinogenic health effects for ACI
OKJ	1.50E+01	1.43E+01	1.48E+01	Unacceptable risk of adverse non-carcinogenic health effects for ACI
MBR	1.50E+01	1.43E+01	1.48E+01	Unacceptable risk of adverse non-carcinogenic health effects for ACI
BAJ	1.34E+01	1.28E+01	1.33E+01	Unacceptable risk of adverse non-carcinogenic health effects for ACI
AKR	1.55E+01	1.48E+01	1.53E+01	Unacceptable risk of adverse non-carcinogenic health effects for ACI
IDR	1.64E+01	1.57E+01	1.62E+01	Unacceptable risk of adverse non-carcinogenic health effects for ACI
MGW	1.55E+01	1.48E+01	1.53E+01	Unacceptable risk of adverse non-carcinogenic health effects for ACI
AGW	1.77E+01	1.70E+01	1.76E+01	Unacceptable risk of adverse non-carcinogenic health effects for ACI
IGW	1.59E+01	1.53E+01	1.58E+01	Unacceptable risk of adverse non-carcinogenic health effects for ACI
CGW	1.34E+01	1.28E+01	1.33E+01	Unacceptable risk of adverse non-carcinogenic health effects for ACI
Ni				
Sample location	Adults	Children	Infants	Health risk
OKC	4.98E-01	4.78E-01	4.93E-01	No obvious non-carcinogenic adverse health risk for ACI
AWR	1.96E-01	1.88E-01	1.94E-01	No obvious non-carcinogenic adverse health risk for ACI
BAK	3.80E-01	3.65E-01	3.77E-01	No obvious non-carcinogenic adverse health risk for ACI
OKJ	4.37E-01	4.19E-01	4.33E-01	No obvious non-carcinogenic adverse health risk for ACI
MBR	4.59E-01	4.40E-01	4.55E-01	No obvious non-carcinogenic adverse health risk for ACI
BAJ	3.80E-01	3.65E-01	3.77E-01	No obvious non-carcinogenic adverse health risk for ACI
AKR	1.74E-01	1.67E-01	1.72E-01	No obvious non-carcinogenic adverse health risk for ACI
IDR	1.44E-01	1.38E-01	1.43E-01	No obvious non-carcinogenic adverse health risk for ACI
MGW	2.17E-03	2.09E-03	2.15E-03	No obvious non-carcinogenic adverse health risk for ACI
AGW	1.96E-01	1.88E-01	1.94E-01	No obvious non-carcinogenic adverse health risk for ACI
IGW	2.17E-03	2.09E-03	2.15E-03	No obvious non-carcinogenic adverse health risk for ACI
CGW	2.17E-03	2.09E-03	2.15E-03	No obvious non-carcinogenic adverse health risk for ACI
Pb				
Sample location	Adults	Children	Infants	Health risk
OKC	1.88E+01	1.81E+01	1.86E+01	Unacceptable risk of adverse non-carcinogenic health effects for ACI
AWR	1.09E-01	1.04E-01	1.08E-01	No obvious non-carcinogenic adverse health risk for ACI
BAK	1.24E+01	1.19E+01	1.23E+01	Unacceptable risk of adverse non-carcinogenic health effects for ACI
OKJ	8.72E+00	8.36E+00	8.63E+00	Unacceptable risk of adverse non-carcinogenic health effects for ACI
MBR	8.31E+00	7.97E+00	8.22E+00	Unacceptable risk of adverse non-carcinogenic health effects for ACI
BAJ	9.05E+00	8.68E+00	8.96E+00	Unacceptable risk of adverse non-carcinogenic health effects for ACI
AKR	1.09E-01	1.04E-01	1.08E-01	No obvious non-carcinogenic adverse health risk for ACI
IDR	3.27E+00	3.14E+00	3.24E+00	Unacceptable risk of adverse non-carcinogenic health effects for ACI
MGW	2.21E+00	2.12E+00	2.18E+00	Unacceptable risk of adverse non-carcinogenic health effects for ACI
AGW	3.27E+00	3.14E+00	3.24E+00	Unacceptable risk of adverse non-carcinogenic health effects for ACI
IGW	1.93E+00	1.86E+00	1.92E+00	Unacceptable risk of adverse non-carcinogenic health effects for ACI
CGW	1.93E+00	1.86E+00	1.92E+00	Unacceptable risk of adverse non-carcinogenic health effects for ACI
NO_3^-				
Sample location	Adults	Children	Infants	Health risk
OKC	6.52E-03	6.26E-03	6.46E-03	No obvious non-carcinogenic adverse health risk for ACI
AWR	5.98E-03	5.74E-03	5.92E-03	No obvious non-carcinogenic adverse health risk for ACI
BAK	8.42E-03	8.08E-03	8.34E-03	No obvious non-carcinogenic adverse health risk for ACI
OKJ	6.25E-03	6.00E-03	6.19E-03	No obvious non-carcinogenic adverse health risk for ACI
MBR	5.98E-03	5.74E-03	5.92E-03	No obvious non-carcinogenic adverse health risk for ACI
BAJ	7.88E-03	7.56E-03	7.80E-03	No obvious non-carcinogenic adverse health risk for ACI
AKR	7.07E-03	6.78E-03	6.99E-03	No obvious non-carcinogenic adverse health risk for ACI
IDR	1.66E-02	1.59E-02	1.64E-02	No obvious non-carcinogenic adverse health risk for ACI
MGW	1.03E-02	9.91E-03	1.02E-02	No obvious non-carcinogenic adverse health risk for ACI

(*continued on next page*)

Table 4 (*continued*)

Mn				
Sample location	Adults	Children	Infants	Health risk
AGW	1.25E-02	1.20E-02	1.24E-02	No obvious non-carcinogenic adverse health risk for ACI
IGW	8.04E-02	7.72E-02	7.96E-02	No obvious non-carcinogenic adverse health risk for ACI
CGW	1.14E-02	1.09E-02	1.13E-02	No obvious non-carcinogenic adverse health risk for ACI

[a] ACI = Adults, Children, and Infants.

3.5. *Potential ecological risk index*

The potential ecological risk index (PERI) assesses the environmental behaviour of heavy metal contaminants and their potential ecological and environmental effects on toxicology [53]. The contamination factor for surface and groundwater samples ranged from 56.62 to 242.35 and 34.78 to 101.57, respectively. PERI ranged from 1.61×10^3 to 2.64×10^3 and 8.10×10^2 to 2.21×10^3 for surface and groundwater, respectively. The magnitude of contamination was in the order Pb > Cd > Ni > Mn and Cd > Pb > Ni > Mn for surface water and groundwater, respectively. The degree of heavy metal contamination in water for all samples was thus categorized as very high, and the ecological risk effect was extremely high. For surface water, the ecological risk of heavy metals was in the order Okrika Creek > Okrika Jetty > Marine base River > Bakana Creek > Idu River > Bakana Jetty > Akabta River > Ahoada west river, and groundwater was in the order Akabta GW > City Centre GW > Marine base GW > Idu GW. Both surface and groundwater in the study sites were heavily susceptible to contamination, with a high ecological risk index due to illegal mining. The potential ecological risk and effect are presented in Table 3.

3.6. *Human health risk model*

The human health risk model based on the hazard quotient (HQ) is a significant tool to estimate non-carcinogenic health risks among infants, children, and adults (ACI). The HQ assesses the vulnerability of different age groups within the study area who may be susceptible to contaminated water ingestion. From the research data, Mn, Ni and NO_3^- had no obvious non-carcinogenic adverse health risk for ACI at all sampling locations. Cd had an unacceptable risk of adverse non-carcinogenic health risk for ACI for all sampling locations. The health risk was in the order of adults > infants > children. HQ for Cd for ACI was highest at Idu River for surface water samples and Akabta groundwater for groundwater samples. For all sampling locations, the HQ for Cd ranged from 13.1 to 17.7, 12.6 to 17.0, and 13.0 to 17.6 for adults, children, and infants respectively. HQ for Pb for ACI was generally highest at Bakana Jetty. Overall, 17% of sampling locations had no obvious non-carcinogenic adverse health risk and 83% had unacceptable risk of adverse non-carcinogenic health effects for Pb for ACI. The health risk of Pb was in the order of adults > infants > children. Table 4 shows the calculated human health risk for ACI for all sampling locations.

3.7. *Principal component analysis (PCA)*

In this study, physicochemical water quality data of surface and groundwater was standardized for PCA. The Kaiser-Meyer-Olkin measure of sampling adequacy was applied, and Bartlett's test of sphericity was significant at $p < 0.05$. Varimax rotation with Kaizer

Table 5
Rotated component matrix.

	Surface water		Groundwater		
	PC1 (50.51%)	PC2 (16.00%)	PC1 (51.39%)	PC2 (26.29%)	PC3 (16.58%)
pH	0.479	**0.802**			
Temp (°C)	−0.118	**−0.747**		0.351	**−0.822**
Turb (NTU)				0.411	**0.656**
EC (μS/cm)	**0.923**	0.357	**0.994**		
TDS (mg/L)	**0.920**	0.361	**0.996**		
BOD (mg/L)	**0.896**				
DO (mg/L)	0.293	**−0.611**			
Salinity (‰)	**0.911**	0.398	**0.984**		
TH (mg $CaCO_3$/L)			**0.882**	−0.381	
Alk (mg $CaCO_3$/L)	**0.779**	0.312	**0.978**		
Cl^- (mg/L)	**0.938**	0.159			
SO_4^{2-} (mg/L)	**0.871**	0.422		**−0.859**	0.473
NO_3^- (mg/L)	−0.252	−0.389	**0.987**		
PO_4^{3-} (mg/L)	0.357	**0.787**	**0.842**	−0.325	
Mn (mg/L)		**0.857**	**−0.953**		
Fe (mg/L)	0.431	−0.223	0.356		**0.91**
Cd (mg/L)	**−0.619**			**0.868**	0.437
Ni (mg/L)	0.164	0.304		**0.965**	
Pb (mg/L)			−0.303	**0.941**	

normalization was applied. Eigenvalues and scree plots were considered in determining the number of principal components. For surface water quality data, two main principal components, PC1 and PC2, explained 66.51% of the variance in the observed water quality with eigenvalues 8.08 and 2.56, respectively. PC1, with the largest eigenvalue, explained 50.51% of the observed water quality variations, and PC2 explained 16.00%. PC1 had strong positive loadings on EC, TDS, BOD, salinity, alkalinity, Cl^-, SO_4^{2-}, and Cd. The high loadings of EC typically indicate the active influence of dissolved ions. The component variables are mainly of anthropogenic origin. PC2 had strong positive loadings on pH, PO_4^{3-}, and Mn and negative loading on temperature and DO. Natural occurrences primarily influence PC2 variables. For example, the dissolution or dissipation of oxygen in surface water is temperature dependent. Additionally, interactions between soil-water-underlying riverbeds interactions due to weathering are natural occurrences that influence the release of Mn and inorganic PO_4^{3-} into surface waters. For groundwater quality data, three principal components explained the observed variations in water quality data. PC1, PC2 and PC3 cumulatively explained 94.26% of the variations, of which 51.39% is attributed to PC1, 26.29% to PC2, and 16.58% to PC3. PC1 had strong positive loadings on EC, TDS, salinity, total hardness, alkalinity, NO_3^-, and PO_4^{3-}. PC2 had strong positive loadings on Cd, Ni, and Pb. Illegal mining activities could support Cd, Ni and Pb leaching into groundwater sources. A solid positive loading of turbidity and Fe and a strong negative loading on temperature were observed for PC3. The variables in each principal component are of an equal mix of anthropogenic and natural occurrences, although the variables in PC1 exert a greater magnitude of impact. The rotated component matrix and the component plot in the rotated space are presented in Table 5 and Fig. 4, respectively.

4. Conclusion

This study presented empirical evidence on water sources that needed to be studied in Rivers State. The study estimates the current pollution and water quality status using water quality indices and establishes the potential ecological and human health risks for adults, children, and infants. The physicochemical properties of selected water sources along illegal crude oil refining sites in Rivers State were successfully analyzed for quality and human health risks. The mean pH for surface and groundwater ranged from 5.61 ± 0.15 to 7.34 ± 0.10 and 5.80 ± 0.10 to 6.39 ± 0.13, respectively. Turbidity, TDS, and BOD data for surface water samples exceeded the WHO GV's, but groundwater samples were within. The ionic dominance pattern for anions for surface and groundwater water samples were in the order $Cl^- > SO_4^{2-} > NO_3^- > PO_4^{2-}$. For surface water samples, mean heavy metal concentration was in the order Pb > Ni > Fe > Cd > Mn > Cu and Pb > Cd > Fe > Mn > Ni > Cu for groundwater. Cd and Pb concentrations in surface and groundwater samples

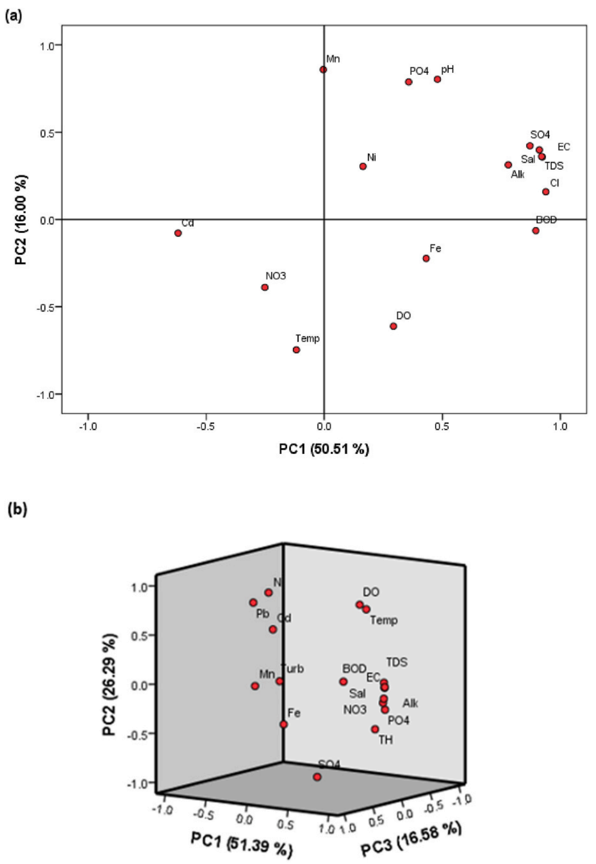


Fig. 4. Component plot in rotated space for (a) surface water and (b) groundwater.

were generally high, with Cd exceeding the WHO GV. The CCME WQI model ranked 62.5% of surface water as marginal, 12.5% as good, 12.5% as poor, and 12.5% as fair. Heavy metals' impact on public health was Pb > Cd > Ni > Fe > Mn. From the Metal index, 25% and 75% of groundwater and surface water samples raise public health concerns. The contribution of heavy metals to surface water pollution was Pb > Cd > Ni > Fe > Mn. The degree of heavy metal contamination in water for all samples was thus categorized as very high, and the ecological risk effect was extremely high. The health risk was in the order of adults > infants > children. Overall, 17% of samples had no obvious non-carcinogenic adverse health risk, and 83% had an unacceptable risk of adverse non-carcinogenic health effects for Pb for adults, children, and infants. For surface water quality data, two main principal components explained 66.51% of the variance in the observed water quality. For groundwater, three principal components explained 94.26% of the observed variations in water quality data. Overall, this study elucidated the impact of illegal mining activities on selected water sources in Rivers State, Nigeria. The study uses water quality and pollution indices to provide evidence of the extent of pollution and the potential human health and ecological risks. Further studies on the impact of illegal oil refining activities on the bioaccumulation of metals on aquatic life are recommended.

Funding

This research was supported with funding from the Ghana Government through the World Bank with Grant number P126974, under the Africa Centres of Excellence (ACE) project.

CRediT authorship contribution statement

Kingsley Onyedika Azuamah: Data curation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing. **Eugene Appiah-Effah:** Conceptualization, Supervision, Writing – review & editing. **Kofi Akodwaa-Boadi:** Formal analysis, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

This study was supported by the Regional Water and Environmental Sanitation Centre Kumasi (RWESCK) at the Kwame Nkrumah University of Science and Technology (KNUST), Ghana. The authors also acknowledge the contribution of the anonymous reviewers and the journal for article publication charge waiver under the research4life initiative.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.heliyon.2023.e20631.

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