



Comparative analysis of groundwater quality statuses and associated health risk indices of metals and total hydrocarbons at locations of tank farm in Delta State, Nigeria

Enuneku Alex Ajeh^a, Odeniyi Olalere Kayode^b, Isibor Patrick Omoregie^{c,*}

^a Department of Environmental Management and Toxicology, Faculty of Life Sciences, University of Benin, PMB 1154, Benin City, Nigeria

^b Ecotoxicology and Environmental Forensics Laboratory, University of Benin, PMB 1154, Benin City, Nigeria

^c Department of Biological Sciences, College of Science and Technology, Covenant University, PMB 1023, Ota, Ogun State, Nigeria

ARTICLE INFO

Handling Editor: Aristidis Tsatsakis

Keywords:

Water quality index
Groundwater
Health risk
Oil exploration
Carcinogenic

ABSTRACT

The study aimed at assessing the groundwater quality and the associated health implications of oil storage tank farms in Asaba, Oghara, Warri, and Koko towns, in Delta State, Nigeria. Fe, Cr, Cd, Ni, Pb, and V concentrations in the groundwater samples were determined using Atomic Absorption Spectrophotometry (AAS), while total hydrocarbons (THC) concentrations were determined using gas chromatography coupled with a flame ionization detector (GC-FID). The quality index of Warri groundwater was 66.38; being within the range of 51–75 was considered poor quality. The water quality indices (WQI) of Oghara, Koko, and Asaba were 163.79, 161.43, and 129.95 respectively, which were all > 100, hence amounting to very poor water quality status. Results indicated that children in Oghara who are orally exposed to chromium are at risk of cancer. Both adults and children orally exposed to THC in Oghara are also at risk of cancer. Furthermore, THC posed an oral route cancer risk to the children in Koko town. The study showed that chromium posed carcinogenic threats to children in Oghara, while THC posed carcinogenic threats to adults and children in Oghara and children alone in Koko. These risks are liable to be mediated through ingestion of the groundwater of Oghara and Koko by the susceptible groups.

1. Introduction

When it rains, some rainwater is taken up by plants, and some water runs off the ground surface to lakes, streams, and other wetlands, while some water evaporates and returns to the atmosphere. In the event of environmental pollution, pollutants are transported through the hydrological cycle. Contaminants in the percolating surface water are transported as leachate plumes, eventually polluting the groundwater [12]. Some precipitation infiltrates the ground and percolates until it reaches the aquifer at a depth where all the fractures, crevices, and pore spaces are saturated with water. Oil spill is a leading cause of water pollution in Nigeria, especially in the oil-producing areas of the Niger Delta. The world environment conference held in Kyoto in 1997 confirmed the drastic need to reduce petroleum waste discharge into the environment [37]. An oil depot is an industrial facility for storing oil and

petrochemical products where these products are transported to end-users or for further storage [1]. Singh et al. [54] pointed out that oil storage tanks have a lifespan of 15–25 years, and the probability that leakage may occur from corrosion increases over time (USEPA, 1997). During the handling and storage of crude oil, spills and leaks may occur due to improper installation, worn-out fittings, corrosion of materials, vandalism or sabotage, and incompetence of oil company personnel constitute the common source of groundwater contamination [20]. When oil spill occurs due to leakage, fuel seeps through the soil to contaminate the groundwater, a vital water resource for drinking, agricultural and industrial use. Constant monitoring of groundwater quality is therefore essential after crude oil exploration and exploitation activities.

Soil and water are the first environmental media that are impacted by pollution from oil exploration activities (Adoki et al., 2007). Oil spill

Abbreviations: LOD, Limit of detection; LOQ, Limit of quantification; THC, Total hydrocarbons; PCA, Principal component analysis; CRI, Cancer risk index; HQ, Harzard quotient; CDI, Chronic daily intake; SF, Slope factor; DACR, Dermal-associated cancer risk; IACR, Ingestion-associated cancer risk; ORCR, Oral route cancer risk.

* Corresponding author.

E-mail address: patrickisibor007@gmail.com (I.P. Omoregie).

<https://doi.org/10.1016/j.toxrep.2022.03.001>

Received 7 June 2021; Received in revised form 28 February 2022; Accepted 1 March 2022

Available online 8 March 2022

2214-7500/© 2022 Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

has been a major environmental issue in Nigeria due to the total reliance of the economy on the oil sector (UNEP, 2011). Adewuyi and Olowu [1] suggested that a leakage rate of two drops per second can result in the loss of almost 500 gallons of fuel in one year and contaminate nearly half a billion gallons of groundwater to the point where its usability is completely compromised. In order to manage fuel leakages in storage tanks, proper installation, leak testing, leak backup containment, and replacement of old tanks are required.

Nigeria is one of the significant crude oil-producing countries where petroleum products are transported through pipelines to several oil depots located all over the country from where mobile tankers transport it to end-users [8]. The environments are contaminated with these products through accidental spills and leakages during loading and offloading tankers in the depots, washing oil storage tanks [1], and deliberate discharge of effluents as a result of sabotage. These significantly contaminate soils and ultimately pollute surface and groundwater through, thereby constituting severe health and environmental hazards to humans and aquatic resources (Uzoekwe et al., 2011; [2]).

Human exposure to heavy metal pollution has risen dramatically as a result of an exponential increase in their use in several industrial, agricultural, domestic and technological applications, which has led to the wide distribution in the environment thus raising concerns over their potential effect on human health [58]. The toxicity of heavy metals depends on several factors including the dose, route of exposure and chemical species, age, gender, genetics, and the nutritional status of exposed individuals.

Hemoglobin constitutes two-thirds of the body's iron content. Iron is utilized in the mitochondrial electron transport chain for energy metabolism and other homeostatic processes. Exposure to excess iron through the skin or mouth promotes hydroxyl radicals and other reactive oxygen species that damage vital cellular components such as DNA, lipids, and cell membranes. Excess iron in the circulatory system may result in anemia and hemochromatosis in extreme cases. A hemochromatotic individual accumulates excess iron from the liver's circulatory system to form fibrosis, cirrhosis, cardiovascular and pancreatic dysfunction [59].

In developing countries, apart from fossil fuel, other lead sources include boat construction, lead-based paint products, batteries, grid, pigments, etc. Due to the non-biodegradability of lead, its highly persists in the environment, causing several ecophysiological hazards. Lead toxicity is a severe ecotoxicological disease as it impacts the entire human system. Studies have shown that lead mainly exerts its deleterious effects on the nervous system in children and adults. However, the severity of the damages to the system is more significant in children than adults [66]. Prolonged exposure of adults to lead can result in impaired cognitive performance [4], while in children, even low concentrations can cause behavioral challenges and hampered intelligence quotient [51]. Chronic toxicity of lead includes infertility, neurotoxicity, anemia, and increased blood pressure in old and middle-aged individuals. In extreme cases, severe damage to the brain and kidneys of adults and children; and eventuality death have been recorded. In pregnant women, high exposure to lead may cause miscarriage or low weight in neonates [66].

Despite its fatal toxicity, cadmium is still used in batteries, electroplating, paint manufacture, plastic products, acrylic colors, watercolor pigments, blue ultraviolet light in fluorescent microscopes, and crude oil exploration [32]. Crude oil contains cadmium that may contaminate soil, and leachate plume may pollute the groundwater. The oral route is the primary exposure of man to cadmium. Studies have shown that plants in non-industrial areas contain less cadmium, but animals and humans in such areas contain high cadmium levels due to biomagnification through the food chain via cadmium dissolved in groundwater. Cadmium in a river may flow downstream to contaminate seafood. Humans, the ultimate predators, are exposed to the risk of cadmium poisoning through alimentation.

Itai-tai disease in plant disease caused by cadmium due to cultivation

using cadmium-contaminated water [43]. Cadmium toxicity is initiated through apoptosis, oxidative stress, and DNA damage. The most documented cadmium-related toxicity, however, is oxidative stress. A study on chronic exposure of Wister rats to cadmium showed hepatotoxicity and nephrotoxicity, induced by inhibition of the cellular antioxidant system's component [11,52]. Oxidative stress further activates the transcriptional activity of the metallothionein coding genes. Metallothionein, which is an abundant protein in animals, further forms a complex called cadmium-metallothionein [6] in a reaction that can be accelerated by an increase in temperature, particularly in the kidney. This complex accumulates in the tubules via reuptake, causing conformation changes in renal tubular cells and disruption of glomerular cell functions. The disruption in the kidney functions leads to hampered calcium metabolism, increasing the organ's calcium load, causing kidney stones and ultimately cancer.

Furthermore, disruption of calcium metabolism may cause bone damage. Elevated cadmium concentration in the kidney is directly linked to increased excretion of cadmium in the urine and decrease of the same in bones, where it is required. Cadmium exposure may result in bone pain, osteoporosis, and tai-tai disease [29,56,7]. Cadmium may also act as an endocrine disrupter in the reproductive system [28]. It mimics the divalent state of zinc, thereby binding to the zinc-binding site on DNA. Cadmium can disrupt the ovarian steroidogenic pathway, progesterone, and testosterone production. It mimics endogenous estrogen, thus increasing the risk of ovarian cancer and breast cancer [22, 27].

Chromium is ubiquitous in the earth's crust, and its chemical state is a function of its toxicity. Although chromium exists in divalent to hexavalent compounds, only the trivalent and hexavalent chromium compounds elicit substantial biological toxicity. Sources of anthropogenic chromium include chromite ore mining, paints, pigment production, tanning of leather, formation of wood preservatives, anticorrosive agents, and crude oil exploration [34]. These sources are responsible for chromium contamination of soil, surface, and groundwater. In animals' circulatory systems, chromium compounds are reduced from hexavalent to trivalent, producing reactive hydroxyl radicals. Mechanisms of chromium toxicity include generations of apoptosis, reactive oxygen species, oxidative stress, and DNA damage. These physiological perturbations may result in dermatitis, nephrotoxicity, malignant tumor, and cancer.

Nickel is widely used for diverse industrial applications, including alloys and various pigments. Nickel contaminates soil and groundwater from mining, smelting, and crude oil exploration processes. The routes of man's exposure to nickel include inhalation, dermal and oral. Industrial dust from nickel refineries includes water-soluble nickel compounds such as Ni_3S_2 , and NiO , which are carcinogenic. Although the carcinogenic molecular mechanism of nickel is not well understood, studies, however, suggest that nickel exposure induces oxidative stress through overwhelmed antioxidant enzymes, DNA methylation, and DNA double-strand breaks [13,31,36] which may result in hepatotoxicity, nephrotoxicity, and cancer [32].

Vanadium is ubiquitous in soil, water, and air. Natural sources of atmospheric vanadium include continental dust, marine aerosol, and volcanic eruptions. Environmental contamination with vanadium is mainly from industrial sources, especially oil refineries and power plants that use vanadium-rich fuel oil and coal. Anthropogenic sources of vanadium are greater than those released from natural sources. Pollution of water with vanadium is often greater than atmospheric pollution. The transport and partitioning of vanadium in water and soil is influenced by the background factors such as the acidity of the water or soil and particulates. Vanadium can either be dissolved in water as ions or become adsorbed to particulate matter.

Hydrocarbons are compounds comprised of hydrogen and carbon atoms. They are classified as either aromatic (cyclic) or aliphatic (straight-chained), typically the chief components in crude oil. Oral and dermal exposure to crude oil can cause significant health risks such as

diseases, systemic toxicity, morbidity, and mortality [10,5,55,9]. Metal toxicity depends on compound properties, viscosity, surface tension, volatility, and additives.

There is a paucity of information on health hazards associated with metals and hydrocarbon contamination of groundwater at oil depots in Nigeria. The study thus aimed at assessing the groundwater quality and the associated health risks posed by Fe, Mn, Zn, Cu, Cr, Cd, Ni, Pb, V, and total hydrocarbon (THC) in the groundwater at selected storage tank farms in Warri, Oghara, Koko, and Asaba, Delta State, South-Southern Nigeria.

2. Materials and methods

2.1. The study area

The study was conducted in towns where tank farms are located in Delta State, Nigeria, namely; Warri, Oghara, Koko, and Asaba. Four (4) stations were designated in each town, from which replicate estimations were computed for accuracy.

All four stations are within the tropical rainforest in Delta State, South-Southern Nigeria (Fig. 1). The towns are interspersed with patches of mangrove forest along the coast and coastal wetlands. The region has a bimodal rainfall pattern, averaging 1600 mm per year. The two rainfall peaks fall between May- July, and September- October. The region also experiences intermittent minor rains all year round. The humidity of the region ranges from 70% to 90%.

2.2. Collection of groundwater samples

Water samples were collected from 16 sub-stations (4 per town/station) during the periods of November 2018- April 2019. They were collected from boreholes and private water wells. Samples were collected from each point twice each month for a months. At each sampling point, groundwater samples were collected in a 500 mL plastic bottle that was cleaned with 10% nitric acid, rinsed thoroughly with distilled water, and oven-dried (APHA, 2005). All the samples were well labeled, stored in an ice chest, and transported to the Microbiology Laboratory of the Petroleum Training Institute, Effurun Delta State, Nigeria.

2.3. Determination of toxicant concentrations

2.3.1. Determination of metal concentrations

The groundwater samples were digested with 0.5% nitric acid (HNO₃) at a pH of 2.0. The essence of acidification of collected water samples is to minimize the precipitation and adsorption on the walls of the container [40] and prevention of microbial activity .

Metal concentrations were determined using Absorption Spectrophotometer (PINAAcle 900 T Perkin Elmer) and calculated thus;

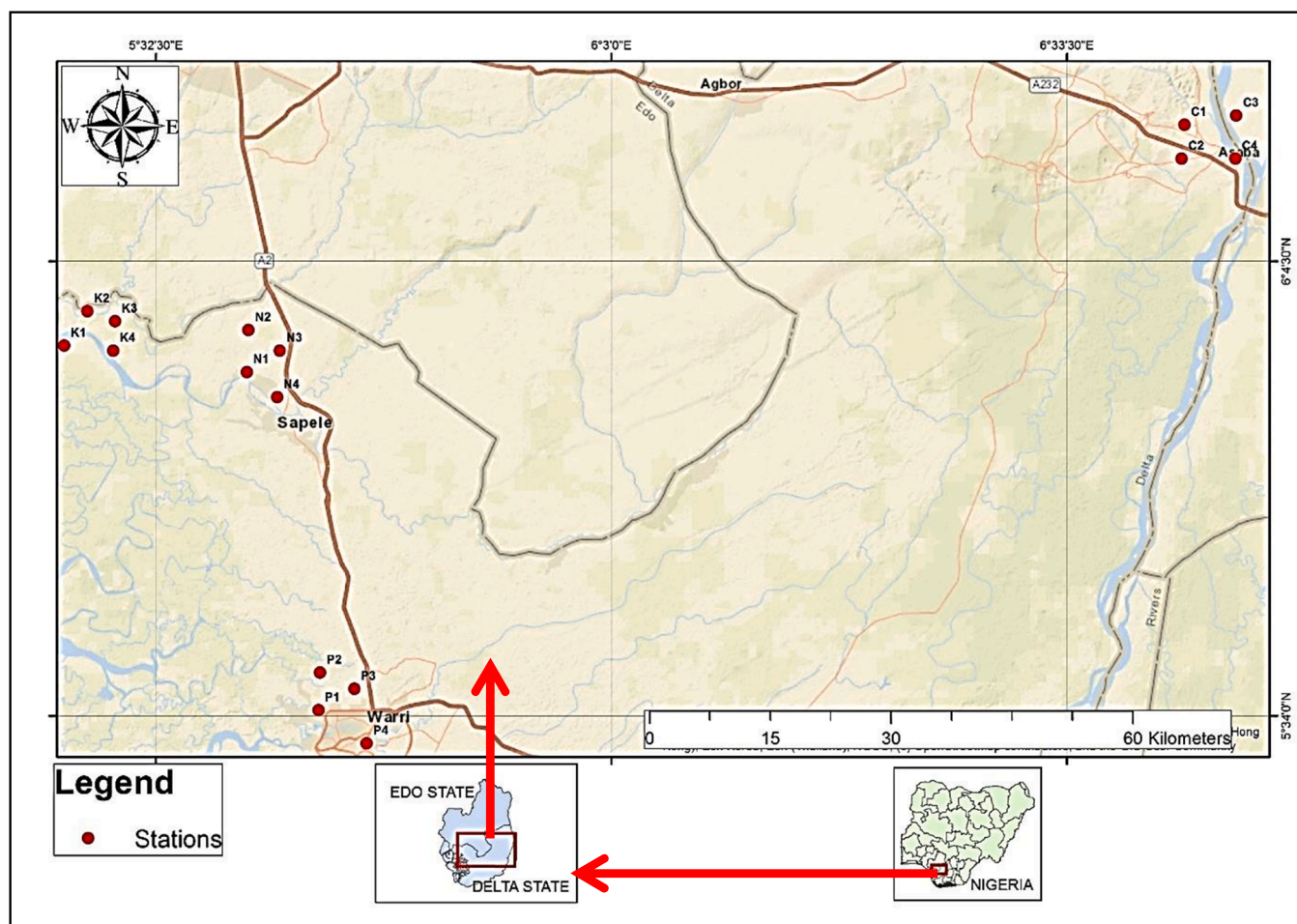
$$\text{Final Conc. (mg/kg)} = \text{Conc. (analytical measurement)} \times \text{Volume of extract} / \text{sample weight (grams)}$$


Fig. 1. Map of the study area showing sampled stations, Map designed using QGIS software version 3.10.1 'A Coruña' (QGIS Development Team³¹), URL: <https://qgis.org/en/site/forusers/download.html#>.

2.3.2. Determination of THC concentrations

Hydrocarbons were extracted from water samples using a stationary phase of separation, HP-5 capillary column coated with 5% phenyl methyl siloxane (30 m length x 0.32 mm diameter x 0.25 µm film thickness) (Agilent Technologies). Agilent 7890 B gas chromatography coupled to flame ionization detector (GC-FID) was used for the determination of total hydrocarbons at 254 nm. After calibration, water samples were analyzed, and corresponding total hydrocarbons concentrations were obtained [25].

2.4. Determination of water physicochemical parameters

The physicochemical parameters such as the biological oxygen demand (BOD), pH, electrical conductivity (EC), total suspended solids (TSS), and total dissolved solids (TDS) were determined using a multi-parameter probe (Horiba Water Checker Model, U10) and recorded in-situ.

2.5. Quality control and quality assurance measures

Sampling bottles were pre-cleaned using 65% ethanol and sterilized at 120 °C for 20 min, using a pressure steam sterilizer (Model: SM280E), purchased from Surgifriend Medicals, England. Sterile laboratory gloves and other personal protective equipment were used throughout the laboratory session. All readings were taken in triplicates to enhance accuracy.

2.5.1. Validation of trace metals

The precision and accuracy of the AAS were validated by repeating the procedures thrice. Certified reference materials (CRM) by Federal Environmental Protection Agency (2003) were adopted as a guide. The recovery rates ranged from 91% to 96%, relative standard deviation (SD) was < 6% (ascertained by Microsoft Excel, 2010), indicating high data reliability. The reference solutions used to obtain the calibration curves were prepared from a stock solution containing 1000 mg/L of each analyzed metal.

The limits of detection (LOD) and the limits of quantification (LOQ) were estimated with the standard deviations of 30 repeated readings obtained for the analytical blanks and slopes of the analytical curves ($LOD = 3\sigma/slope$ and $LOQ = 10\sigma/slope$). The LODs were Fe = 0.04–0.07 µg/L, Pb = 0.07–0.12 µg/L, Zn = 0.02–0.04 µg/L, Cu = 0.06–0.12 µg/L, Mn = 0.04–0.12 µg/L, Cr = 0.04–0.12 µg/L, Cd = 0.06–0.12 µg/L, Ni = 0.07–0.12 µg/L.

2.5.2. Validation of THC

Total hydrocarbon readings of the GC-FID were validated by the certificate (No. TPH-R3-SET, by AccuStandard). The linearity (tested between 0 and 5.6 µg/L) of the calibration range was determined to ascertain the accuracy of the equipment. The coefficient of variation of the results was validated using LODs and LOQs. The LODs and LOQs were calculated from the blank and analyzed by the GC-FID. The limit of detection was calculated using triplicate readings.

2.5.3. Compliance statement

All experimental procedures were performed in accordance with standard scientific guidelines and regulations. Methods were carried out in accordance with relevant guidelines and regulations.

2.6. Statistical analysis

The trace metals and THC concentrations in 72 water samples were reported as mean ± standard deviation (SD). These descriptive statistics were subjected to analysis of variance (ANOVA) to test for the significant differences at a probability level of 0.05. They were further subjected to a posthoc Tukey test at a 95% confidence interval and a probability level of 0.05 using SPSS (version 20). The Kaiser-Meyer-Olkin (KMO) analysis

was conducted on the contaminants' concentrations to validate the sampling adequacy and usability.

The data's sphericity was analyzed using Bartlett's test, which gave a significant p-value of 0.026, indicating that a factor may be responsible for the variability in the data analyzed [26].

2.6.1. Principal component analysis

Principal component analyses were conducted for the metals and THC in the different groundwater samples using SPSS (version 20). Eigenvalues were obtained for the toxicant concentrations in the groundwater samples through communality extractions. An eigenvalue of 1 was adopted as the significant value for the components. Oblimin with Kaiser Normalization was used in analyzing the significant components obtained from the PCA for Warri, Oghara, and Koko, based on the oblique output from KMO and Bartlett's analyses [26]. Varimax rotated matrix was used in the case of Asaba as the data obtained was oblique. The components were represented on scree, and 3-dimensional scatter plots for ease of spatial visualization and analysis of the data.

Cluster analysis was determined among the parameters in the sampling points using average linkage hierarchical clustering to evaluate inter-relatedness of toxicity occurrence at the respective locations.

2.6.2. Health risk estimations

Health risks were assessed using indices such as hazard quotient (HQ) and cancer risk index (CRI), which were computed for adults (male and female) and children using values adopted from referenced literature (Table 1).

Carcinogenic risk of the groundwater was calculated thus: [60].

Cancer risk index (CRI) = CDI X SF

CDI = chronic daily intake dose of carcinogens (mg/kg/d) for dermal and ingestion, while SF = carcinogenicity slope factor (mg/kg/d). Among the metals analyzed, cadmium, chromium, and nickel are classified as category 1 carcinogenic trace metals by the [24]. The cancer slope factors assigned to the toxicants analyzed were THC = 25, Cd = 0.38, Cr = 0.5, Ni = 1.7, Pb = 0.0085 mg/kg-d⁻¹ [24]. Other metals such as Fe, Mn, Zn, V, and Cu were assigned zero (0) as no data of their potential carcinogenicities are available in the literature.

Furthermore,

$CDI_{dermal} = CW \times AF \times SA \times DAF \times CF \times EF \times ED$ [23]

BW x AT

$CDI_{ingestion} = CW \times IR \times CF \times EF \times ED$ [60]

BW x AT

CDI = chronic daily intake dose, CW = concentration of toxicant in water (mg/L); IR = water ingestion rate (L/day), CF = conversion factor

Table 1

Adopted indices for health risk calculations on trace metals and THC.

Adopted indices	Adults		Children		Reference
	Male	Female	Reference	Reference	
Water ingestion rate (mg/kg)	100	100	[62]	200	[62]
Body weight (kg)	70	65	[30]	10	[61]
Conversion factor (kg/mg)	10 ⁻⁶	10 ⁻⁶	[60]	10 ⁻⁶	[60]
Surface area of skin (cm ²)	215	188	[61]	184	[61]
Dermal absorption factor	0.13	0.13	[60]	0.13	[60]
Exposure frequency (day/year)	350	350	[62]	350	[62]
Exposure duration (days/year)	30	30	[47]	6	[47]
Average time (day)	8760	8760	[23]	2190	[23]
Skin adherence factor (mg/cm ²)	0.2	0.2	[41]	0.2	[41]

(kg/mg), EF = Exposure frequency (day/year), ED = exposure duration (years), BW = body weight (kg), AT = average time (day), AF = Skin adherence factor (mg/cm²), EA = exposed surface area of skin (cm²), DAF = dermal absorption factor.

On the other hand, non-carcinogenic health risks were estimated using hazard quotient (HQ), which was calculated thus: [23].

$$HQ = CDI$$

$$RfD$$

Where RfD signified the reference dose; which was separately estimated for the oral and dermal routes. The adopted oral RfDs were Fe = 7.00×10^{-1} , Cd = 1.00×10^{-3} , Pb = 3.5×10^{-3} , Cr = 3.0×10^{-3} , Ni = 2.0×10^{-2} , Cu = 4.0×10^{-2} , Zn = 3.0×10^{-1} , THC 3.52×10^{-3} mg/kg/d. While the adopted dermal RfDs were Fe = 7.00×10^{-1} , Pb = 3.52×10^{-3} , Cd = 1.00×10^{-3} , Cr = 2.86×10^{-5} , Ni = 2.06×10^{-2} , Cu = 4.02×10^{-2} , Zn = 3.00×10^{-1} , THC 0.06 mg/kg/d.

The total hazard quotient for each individual in the exposed population was calculated thus:

$$\sum HQ = HQ_{\text{dermal}} + HQ_{\text{ingestion}}$$

The hazard index (HI) = overall non-carcinogenic risk posed by individual toxicant.

It was calculated thus: [42].

$$\sum HI = HQ_1 + HQ_2 + HQ_3$$

HQ = hazard quotients of the individual metal.

HQ or HI < 1 = insignificant, while ≥ 1 = significant.

The health risk index (HRI) was calculated thus: (U.S. EPA, 2010).

$$HRI = CDI \times SF$$

The slope factor (SF) values for the toxicants were adopted from the standard of USEPA [60].

3. Results

3.1. Analysis of the borehole water quality

The temperatures of the groundwater at Koko and Asaba were significantly higher ($p < 0.05$) than the temperatures of Warri and Oghara (Table 2). However, there was no significant difference in the groundwater's pH across the four sampled locations ($p > 0.05$). The pH values at all the stations were fairly acidic, as they were below the established limit of FME_{Env} (Table 2).

The turbidity, Mn, Cd, and Ni concentrations at Oghara, Koko, and Asaba were significantly higher than those at Warri ($p < 0.05$). The TSS, TDS, Cl, NO₃, Fe, Zn, Cu, Pb, V, and BOD₅ at Oghara and Koko were significantly higher than Warri and Asaba ($p < 0.05$). However, the dissolved oxygen concentration in the groundwater at Warri was higher than the concentrations at Oghara, Koko, and Asaba ($p < 0.05$). Among these, only the Cu concentrations in the groundwater at Oghara and Koko exceeded the FME_{Env} regulatory limit.

The concentrations of Pb in Oghara and Koko's groundwater samples were significantly higher than Asaba, which was higher than Warri ($p < 0.05$). The concentrations of Cr were in the order of Koko > Oghara > Asaba > Warri ($p < 0.05$), while the concentrations of THC were in the order of Oghara > Koko > Asaba > Warri ($p < 0.05$).

The other parameters and metals analyzed neither had a significant difference among the stations nor were up to the regulatory limits.

The adopted format for water quality index (WQI) and the respective water quality status (WQS) was as prescribed by Shweta, et al. (2013). The groundwater quality index at Warri was 66.38; within the range of 51–75 WQI, WQS was poor (Fig. 2). The WQI of Oghara, Koko, and Asaba was 163.79, 161.43, and 129.95, respectively, which were all > 100, hence amounting to WQS of undrinkable.

3.2. Health risk estimations of the groundwater

The dermal-associated hazard quotient of the toxicants in all four study areas' groundwater samples was < 1, hence insignificant (Fig. 3). However, among others Cr had outstanding values in the average child at Oghara > Oghara male > Oghara female > Koko child > Asaba

Table 2

The physicochemical parameters and metal concentrations in groundwater water at 4 host communities' tank farms.

Parameters	Unit	WARRI		OGHARA		KOKO		ASABA		FME _{Env} . (2003)
		MEAN	SD	MEAN	SD	MEAN	SD	MEAN	SD	
Temp	°C	26.09 ^B	0.96	26.53 ^B	0.84	27.01 ^A	0.55	27.72 ^A	0.73	–
pH		5.82	0.48	5.54	0.36	5.77	0.46	5.64	0.42	6–9
Turb.	NTU	3.97 ^B	1.80	5.26 ^A	2.37	5.04 ^A	2.26	4.49 ^A	2.16	–
TSS	Mg/L	5.85 ^B	2.31	8.98 ^A	3.16	8.22 ^A	3.51	6.92 ^B	2.84	–
TDS	Mg/L	59.81 ^B	16.16	79.02 ^A	14.90	79.20 ^A	19.01	65.65 ^B	15.02	2000
DO	Mg/L	6.26 ^A	0.43	5.63 ^B	0.46	5.67 ^B	0.64	5.89 ^B	0.33	–
BOD ₅	Mg/L	2.31 ^B	0.46	3.43 ^A	0.66	3.02 ^A	0.68	2.56 ^B	0.95	30
HCO ₃	Mg/L	22.28	12.92	36.60	10.13	38.78	11.58	29.37	12.66	–
Na	Mg/L	0.86	0.43	0.98	0.22	0.99	0.39	0.94	0.34	–
Cl	Mg/L	24.11 ^B	19.84	30.05 ^A	18.12	35.28 ^A	28.72	25.54 ^B	15.53	–
P	Mg/L	0.68	0.38	0.93	0.53	1.22	0.75	0.85	0.48	–
NH ₄ H	Mg/L	0.09	0.05	0.19	0.09	0.17	0.14	0.12	0.05	–
NO ₂	Mg/L	0.05	0.03	0.14	0.15	0.13	0.16	0.08	0.04	–
NO ₃	Mg/L	1.58 ^B	0.52	2.34 ^A	1.00	2.62 ^A	1.43	1.70 ^B	0.62	–
SO ₄	Mg/L	0.66	0.35	0.93	0.25	0.92	0.33	0.80	0.32	–
Fe	Mg/L	0.63 ^B	0.38	1.33 ^A	0.78	1.40 ^A	1.07	0.87 ^B	0.42	20
Mn	Mg/L	0.07 ^B	0.04	0.14 ^A	0.06	0.11 ^A	0.06	0.10 ^A	0.04	–
Zn	Mg/L	0.24 ^B	0.15	0.56 ^A	0.20	0.54 ^A	0.31	0.38 ^B	0.18	3.0
Cu	Mg/L	0.03 ^B	0.02	0.05^A	0.03	0.06^A	0.04	0.04 ^B	0.03	0.05
Cr	Mg/L	0.01 ^D	0.01	0.03 ^B	0.03	0.04 ^A	0.04	0.02 ^C	0.02	–
Cd	Mg/L	0.01 ^B	0.01	0.03 ^A	0.02	0.03 ^A	0.02	0.03 ^A	0.02	–
Ni	Mg/L	0.00 ^B	0.00	0.01 ^A	0.01	0.01 ^A	0.02	0.01 ^A	0.01	–
Pb	Mg/L	0.01 ^C	0.01	0.03 ^A	0.03	0.03 ^A	0.02	0.02 ^B	0.01	< 1
V	Mg/L	0.00 ^B	0.00	0.01 ^A	0.01	0.01 ^A	0.01	0.00 ^B	0.00	< 1
THC	Mg/L	0.04 ^D	0.03	0.10 ^A	0.03	0.09 ^B	0.05	0.07 ^C	0.03	2

Numbers with superscripts are significantly different. Emboldened numbers are at variance with the established limits. Sample size (N) = 18.

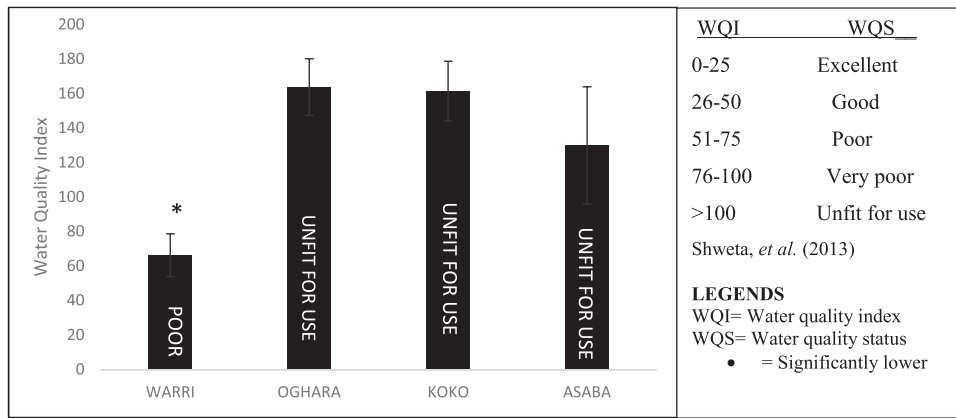


Fig. 2. Comparative water quality analysis of the localities.

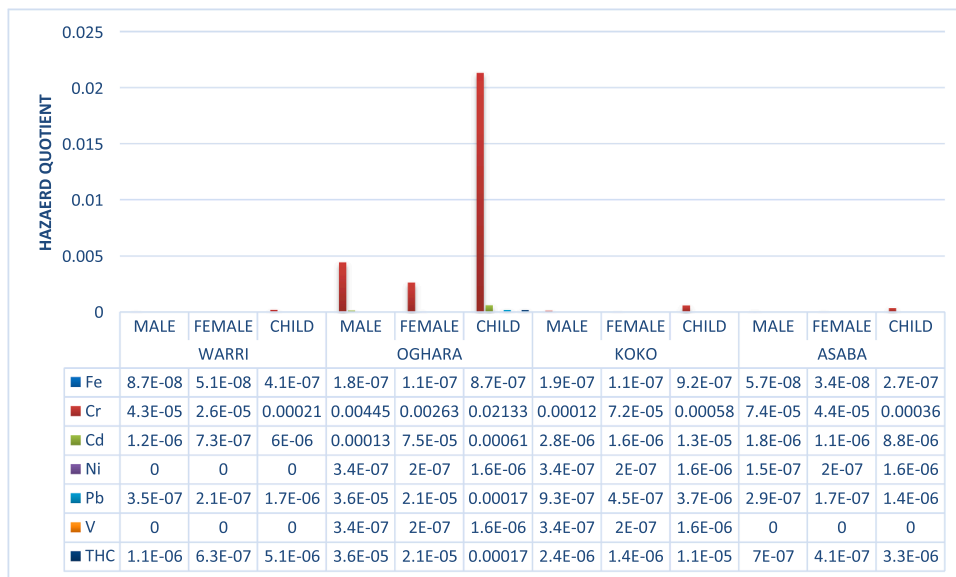


Fig. 3. Dermal-associated hazard quotients of toxicants in the study areas.

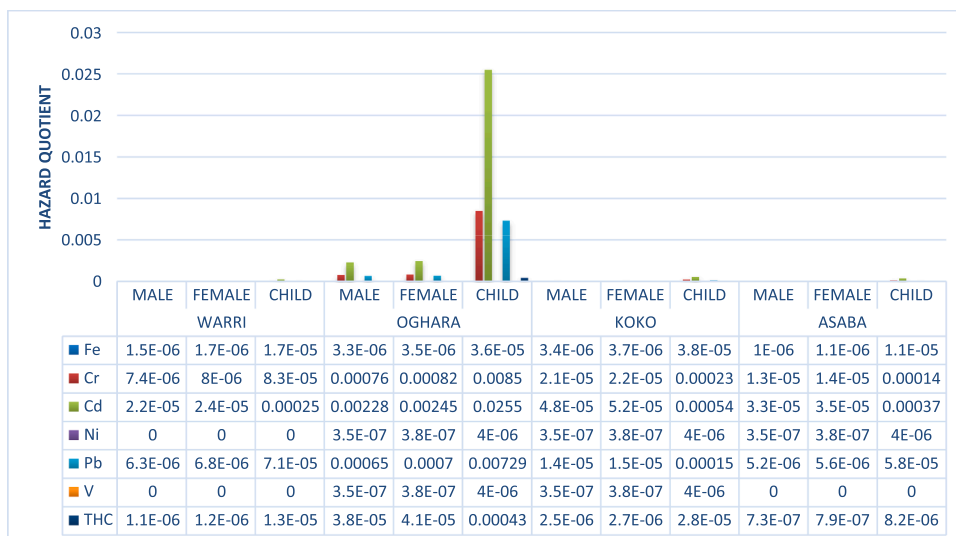


Fig. 4. Ingestion-associated hazard quotients of toxicants in the study areas.

child> Warri child. Concerning oral exposure (Fig. 4), although all values recorded were also < 1, the highest susceptibility, however, occurred in Oghara, mainly in the average child in the order of Cd> Cr> Pb. Nickel was zero (0) in Warri for all ages, while vanadium recorded zero (0) for all ages in Warri and Asaba because the metal concentrations were zero (0) in the groundwater samples at the locations.

The combined effect of oral and dermal exposures to toxicants also exhibited no significant health hazard quotients in males, females, and children across the study areas (Fig. 5). However, among the study areas, Oghara recorded the highest hazards quotients in children and the order of Cr> Cd> Pb> THC.

The limit of carcinogenic risk established by USEPA [60] is 10^{-6} – 10^{-4} . Therefore, the dermal-associated carcinogenic risks estimated across the study areas showed that THC only posed a significant risk to the average Oghara child. Outstanding but insignificant THC dermal exposure risks were also observed in Oghara male> Oghara female> Koko child (Fig. 6). Chromium and cadmium also exhibited though insignificant but outstanding risks in Oghara children. Iron recorded zero (0) throughout because no known slope factor has been assigned to the metal by established authorities.

There was no significant dermal-associated cancer risk (DACR) among all the toxicants across the towns (Fig. 6). However, chromium posed a significant ingestion-associated cancer risk (IACR) to the children only in Oghara, the town where THC posed IACR to the adults and children (Fig. 7). Furthermore, in Koko town, THC posed IACR to the children only.

3.3. Multivariate source allotment for the physicochemical parameters in the groundwater

3.3.1. Principal component analysis (PCA) of Warri groundwater

The proportion of the 17 components extracted from the factor loadings of the dataset (Table 3) yielded significant initial Eigenvalues of 8.255, 3.163, 2.596, and 1.218 for components 1, 2, 3, and 4, respectively. This statistical output was emphasized by the scree plot of the component matrix (Fig. 8). Furthermore, components 1, 2, 3, and 4 comprised percentage variances of 48.557%, 18.607%, 15.270%, and 7.165%; and cumulative percentages of 48.557%, 67.164%, 82.434%, and 89.598% respectively (Table 3). In further processing the data in the extraction sum of the square, components 5–17 were excluded as they were insignificant. Therefore, the resultant rotation sum of square loadings was 6.839, 3.127, 5.871, and 1.693 for components 1, 2, 3, and 4 respectively.

Furthermore, the matrix in the 4 significant components were extracted to determine the activity levels of the parameters in each component (Table 4). The order of dominance in component 1 was Zn (0.948) > Cu (0.945) > Fe (0.936) > Cd (0.916) > Cr (0.897) > Mn

(0.807) > V (0.762) > Ni (0.760) > TDS (0.757). While in component 2 the significant parameters were turbidity (0.959) > TSS (0.931) > THC (0.729) only. There was no significant parameter in component 3 and the only significant parameter in component 4 was DO (0.802).

The correlation matrix of the 4 components showed no significant relationship, indicating independence and high competitiveness, hence the reliability of the processed data (Table 5).

The PCA plot in the rotated space for Warri showed no strong affinity of the parameters analyzed for any of the components (Fig. 9). Generally, the parameters were sparsely distributed. BOD and DO, however, clustered close to iron, copper and cadmium. THC and pH were centralized among the components.

The dendrogram of the data using Ward linkage showed that the parameters were distributed into six significant clusters (Fig. 10). Nickel, vanadium, and lead formed a cluster closest to iron and chromium. These two closest clusters were connected to another farther cluster comprising of manganese, zinc, copper, and cadmium. Farthest on the scale are two clusters at the extreme. One of the clusters comprised of pH DO and water temperature, which were relatively closer to the cluster that constitutes TDS and BOD.

3.3.2. Principal component analysis (PCA) of Oghara groundwater

The proportion of the 17 components extracted from the factor loadings of the dataset (Table 6) yielded significant initial Eigenvalues of 7.287, 2.979, 2.866, and 1.575 for components 1, 2, 3, and 4 respectively (Fig. 11). Furthermore, components 1, 2, 3, and 4 comprised percentage variances of 42.867%, 17.521%, 16.861%, and 9.262%; and cumulative percentages of 42.867%, 60.388%, 77.249%, and 86.511% respectively (Table 6). The extraction sum of squares excluded components 5–17 as they were insignificant. Therefore, the resultant rotation sum of square loadings was 7.049, 3.461, 2.856, and 2.094 for components 1, 2, 3, and 4 respectively.

Furthermore, the matrix in the 4 significant components were extracted to determine the activity levels of the parameters in each component (Table 7). The order of dominance in component 1 was Cr (0.956) > Fe (0.907) > Pb (0.892) > Cd (0.794) > Cu (0.790) > Zn (0.781) > V (0.769) > THC (0.754) > Ni (0.748) > TDS (0.720). While in component 2 the significant parameters were TSS (0.800) only and component 4 was pH only (0.874).

The correlation matrix of the four components showed no significant relationship, indicating no shared influence but high competitiveness, hence the reliability of the data presented (Table 8).

The PCA plot in rotated space for Oghara showed a strong affinity of component 3 for iron, copper, nickel, lead, chromium, vanadium, and DO. Turbidity and TSS drifted in the same direction i.e., towards derived component 3 and component 2, while water temperature and pH drifted between component 2 and component 1. Notably, these two drift directions were away from the other physicochemical parameters and

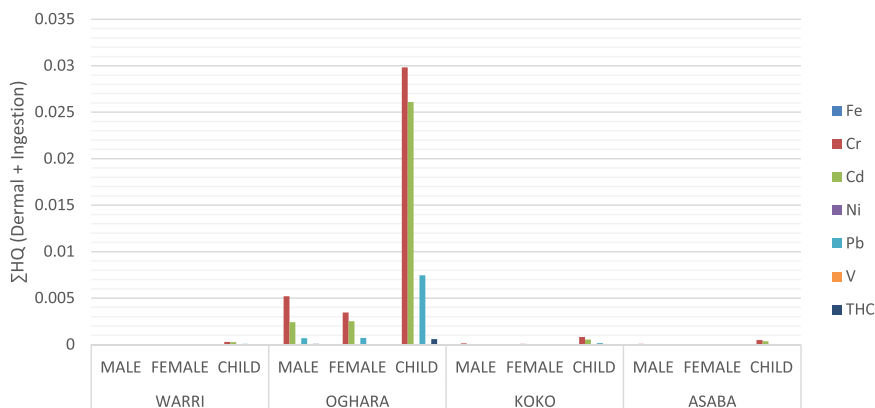


Fig. 5. Comparative combined dermal and oral hazard quotients among the study areas.

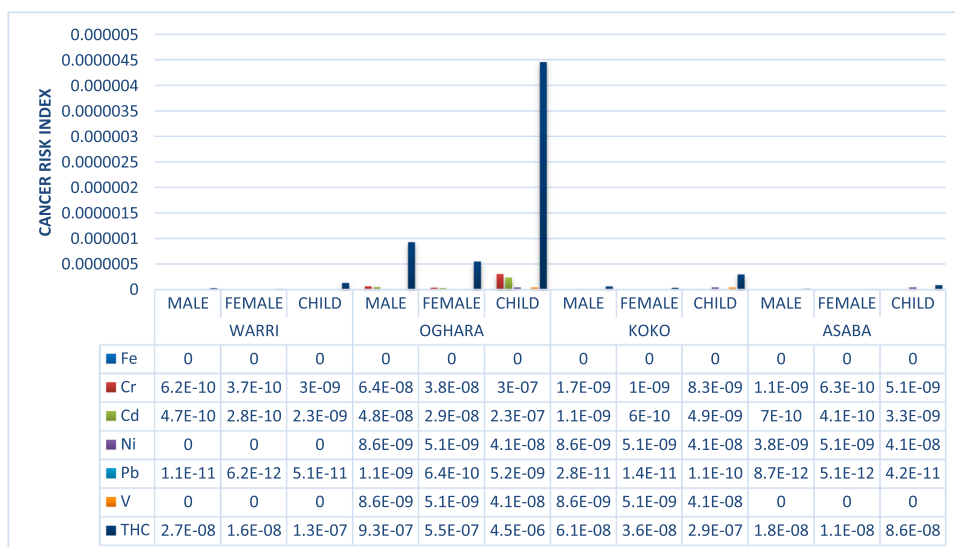


Fig. 6. Dermal-associated cancer risks of toxicants in the study areas.

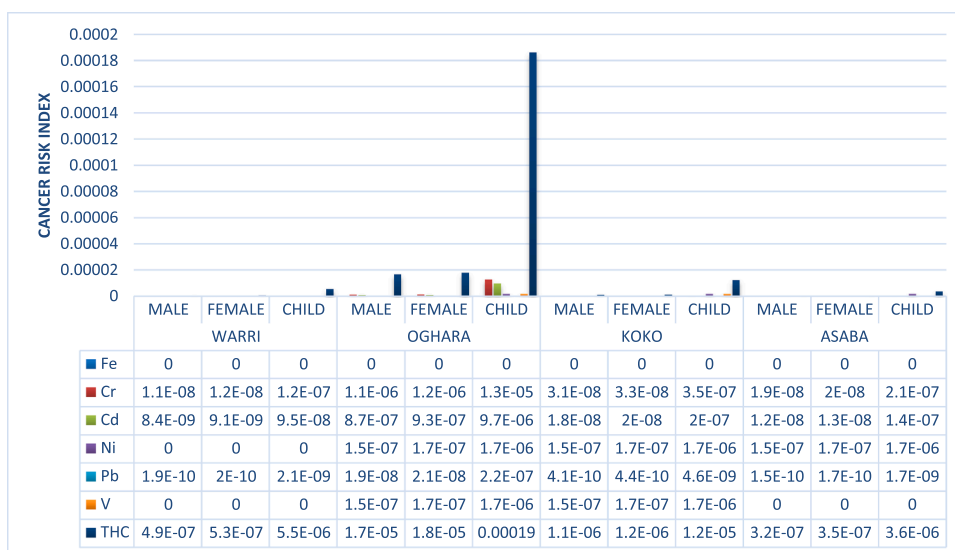


Fig. 7. Ingestion-associated cancer risks of toxicants in the study areas.

toxicants analyzed (Fig. 12).

The dendrogram of Oghara showed 7 main groups. Nickel paired with THC at a farther point than iron paired with copper. Further on the dendrogram scale, both pairs linked up with another cluster of chromium, lead, cadmium, and vanadium at a farther distance and in the highest rank. Farther away by the scale of 25, water temperature, pH, and DO form another cluster linked to a much closer pair of TDS and BOD (Fig. 13).

3.3.3. Principal component analysis (PCA) of Koko groundwater

The proportion of the 17 components extracted from the dataset's factor loadings (Table 9) yielded significant initial Eigenvalues of 8.167, 2.891, 1.802, and 1.406 for components 1, 2, 3, and 4, respectively (Fig. 14). Components 1, 2, 3, and 4 comprised percentage variances of 48.039%, 17.006%, 10.599%, and 8.269%; and cumulative percentages of 48.039%, 65.045%, 75.644%, and 83.913% respectively (Table 9). Furthermore, the extraction sum of squares excluded components 5–17 as they were insignificant. The resultant rotation sum of square loadings was 6.834, 2.579, 5.690, and 1.974 for components 1, 2, 3, and 4.

The matrix in the 4 significant components were extracted to

determine the activity levels of the parameters in each component (Table 10). The order of dominance in component 1 was Cr (0.930) > Pb (0.913) > Fe (0.904) > Cu (0.889) > Cd (0.887) > THC (0.881) > Zn (0.814) > Ni (0.746) > TDS (0.737) > V (0.734) > Mn (0.722). While in component 2 the significant parameters were turbidity (0.810) > TSS (0.804) only. There were no significant parameters in components 3 and 4.

The correlation matrix of the 4 components showed no significant relationship among the components, indicating independence and high competitiveness among the components, hence reliability of the data process (Table 11). The PCA showed that the turbidity and TSS weakly drifted towards components 1. Most of the rest parameters analyzed were evenly central to all the components (Fig. 15).

The dendrogram of the data using Ward linkage showed that the parameters formed 7 clusters. A cluster of iron, zinc, copper, and THC is strongly linked with manganese (Fig. 16). They further linked with two interlinked pairs between turbidity and TSS and; TDS and BOD. At above scale 10 on one hand, these interlinks are further linked up with other cluster comprising nickel and vanadium, ranking highest followed by and linked with chromium, lead, and cadmium. On the other hand,

Table 3
Total variance of parameters in Warri groundwater.

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total
1	8.255	48.557	48.557	8.255	48.557	48.557	6.839
2	3.163	18.607	67.164	3.163	18.607	67.164	3.127
3	2.596	15.270	82.434	2.596	15.270	82.434	5.871
4	1.218	7.165	89.598	1.218	7.165	89.598	1.693
5	.609	3.580	93.179				
6	.524	3.084	96.263				
7	.264	1.555	97.818				
8	.157	.924	98.742				
9	.121	.714	99.456				
10	.065	.380	99.836				
11	.027	.156	99.992				
12	.001	.008	100.000				
13	3.914E-15	2.302E-14	100.000				
14	2.473E-16	1.455E-15	100.000				
15	1.163E-16	6.839E-16	100.000				
16	-1.454E-16	-8.552E-16	100.000				
17	-3.037E-16	-1.786E-15	100.000				

Bold figures indicate parameters with significant values ≥ 1 [24].

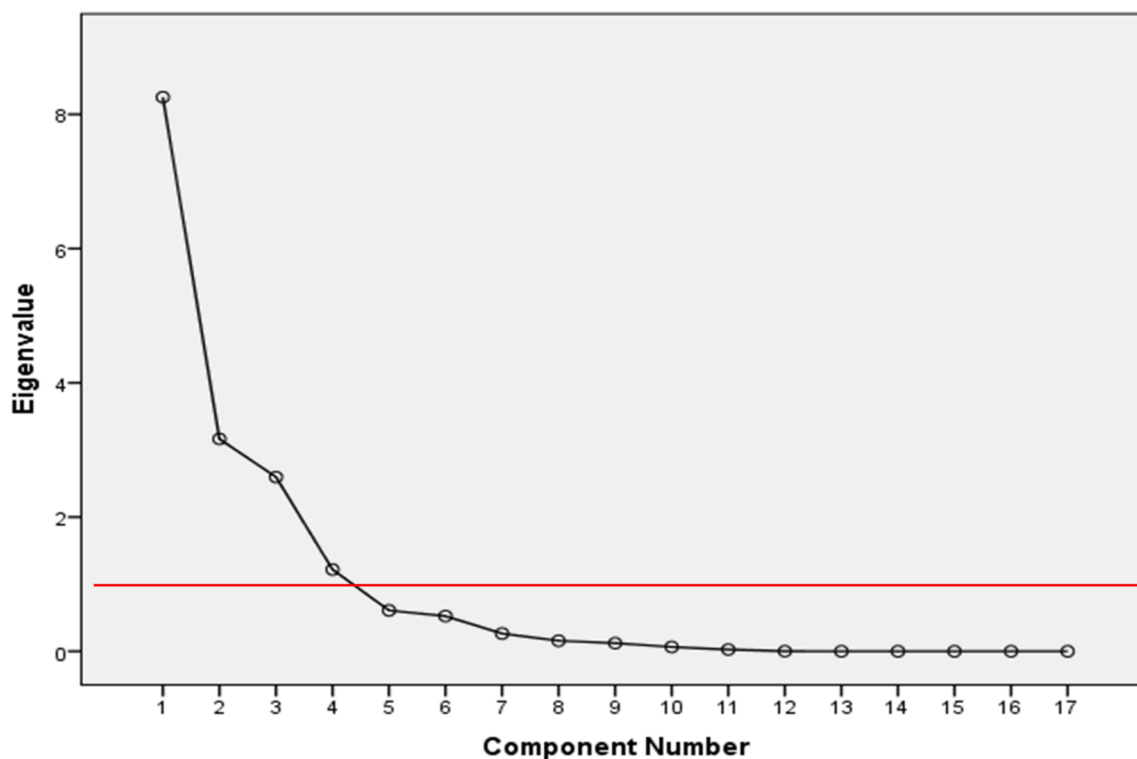


Fig. 8. Scree plot of the component matrix showing significant levels of the Eigenvalues. Redline indicates significant Eigenvalue = 1. (For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)

much farther at scale 25, the interlinks connected to a cluster of pH, DO, and water temperature.

3.3.4. Principal component analysis (PCA) of Asaba groundwater

The proportion of the 17 components extracted from the factor loadings of the dataset (Table 12) yielded significant initial Eigenvalues of 6.841, 2.991, 2.367, 1.314, and 1.146 for components 1, 2, 3, 4, and 5, respectively (Fig. 17). Furthermore, components 1, 2, 3, 4, and 5 had percentage variances of 40.242, 17.597, 13.922, 7.727, and 6.743; and cumulative percentages of 40.242, 57.839, 71.761, 79.488, 86.230% respectively (Table 12). Components 6–17 were excluded in further processing as they were insignificant. Thus, the resultant rotation sum of squares loadings was 3.888, 3.229, 2.963, 2.453, and 2.126 for

components 1, 2, 3, 4, and 5 respectively.

Furthermore, the 5 significant components were extracted to determine the parameters’ activity levels in each (Table 13). The order of dominance in component 1 was Cr (0.885), Ni (0.864), V (0.815), Zn (0.806), Fe (0.804), and Cu (0.754). In component 2 the significant parameters were turbidity (0.887), while the significant parameter in component 3 was TDS (-0.734).

The scatter plot of PCA for Asaba groundwater showed a congregation of most parameters in the center part of the plot, with an indistinct affinity for any component (Fig. 18), except BOD, which drifted towards the derived component 3, and water temperature, which drifted towards component 1.

The dendrogram of the parameters in Asaba groundwater distributed

Table 4
Extracted component matrix of Warri groundwater.

Parameters	Component			
	1	2	3	4
Zn	.948		-.225	.138
Cu	.945	-.163	-.175	
Fe	.936		.150	.237
Cd	.916			
Cr	.897	.146	.271	-.135
Mn	.807	-.186	-.434	.262
V	.762		.619	
Ni				
TDS	.760		.618	
	.757	.174	-.571	.127
pH	-.697	.440	.225	.211
Pb	.632		.507	-.513
Water_Temp	.618	.440	-.454	
Turb		.959		
TSS	.180	.931	-.235	
THC	.393	.729	.387	
BOD	.322	-.477	-.478	-.265
DO		-.303	.438	.802

Bold figures indicate parameters with significant loading factors; > 0.71 [24].

Table 5
Component correlation matrix.

Component	1	2	3	4
1	1.000	-.036	.353	-.150
2	-.036	1.000	.013	-.059
3	.353	.013	1.000	.085
4	-.150	-.059	.085	1.000

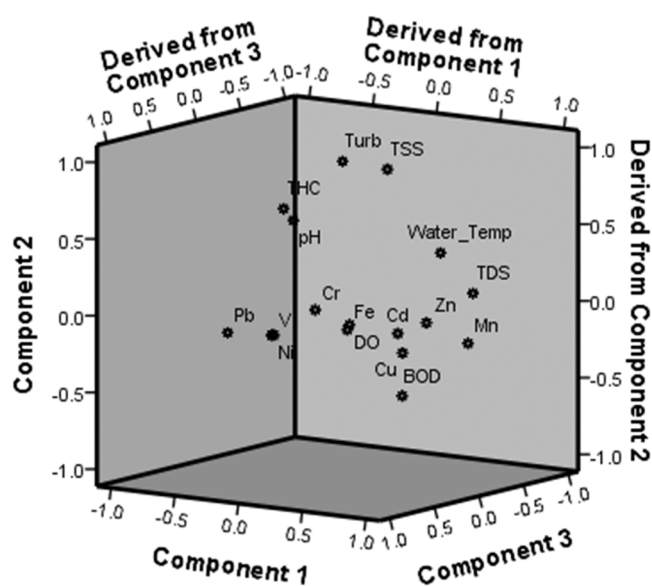


Fig. 9. Principal component analysis plot in rotated space for Warri.

the parameters into a total of 8 groups. Notably, all the metals (except manganese) formed a congregation of clusters below scale 5, which comprised iron, copper, zinc, nickel, vanadium, chromium, cadmium and lead (Fig. 19). They, however linked up with the other physicochemical properties of the water at a distant scale of 25. The sub-clusters among the physicochemical parameters include manganese, THC, and BOD, linked with TDS below 5. These are linked with a pair between turbidity and TSS at a relatively farther scale. Ultimately, at yet a much farther scale of > 10 the clusters connected to water temperature, DO, and pH at the extreme and highest rank.

4. Discussions

4.1. Groundwater quality

Petroleum exploration and production companies use a wide range of chemicals in their operations. These chemicals can pollute the groundwater resource in the areas where such operations are carried out if they are not adequately monitored and controlled according to guidelines and standards set by regulating agencies like the Department of Petroleum Resources (DPR) and Federal Environmental Protection Agency (FEPA) (now Federal Ministry of Environment). In Nigeria, the Department of Petroleum Resources (DPR) was set up to carry out specific oversight functions on oil-producing companies. They ensure that petroleum industry operators do not degrade and or pollute the environment in their operations. They also enforce the clean-up and remediation of oil spills and to acceptable levels.

Evaluating groundwater quality, its suitability for uses, interactions among the contaminants, and the physicochemical ambience parameters and the contaminants' source are all essential in taking decisions on the safest use, management and protection of the vital resource. The permissible pH limit for drinking water is 6.5–8.5 (USEPA, 1990). Outside this range, toxicants associated with health implications may become bioavailable by releasing bonds with other chemicals in complex molecules. However, in this study, the mean pH values for Warri (5.82), Koko (5.54), Oghara (5.77) and Asaba (5.64) indicate slight acidity which may increase the dissociation of metals bounds in complex compounds, hence bioavailability of the trace metals [26]. The pH of the groundwater at Warri being the least acidic partly explains why the WQI and WQS of Warri groundwater were more acceptable than the other locations. Although most of the residents at the study areas use the groundwater for drinking and other domestic purposes, results showed that the groundwater of Warri tank farm may be poor but is much better than those of Koko, Oghara, and Asaba, which are unsuitable for significant purposes. The poor water quality at the tank farms is attributable to the leachate plume resulting from the oil spills [3]. Besides from accidental spills, groundwater contamination by surface storage fuel tanks could be linked to corrosion of steel tanks, faulty installation and operation, and leaking storage tanks. Ayotamuno and Kogbara (2007) pointed out that contaminants from the soil's surface could leach into the subsurface to pollute the groundwater resource at distant locations [45].

Uzoekwe and Oghosanine [63] pointed out that storage tanks have a life of 15–25 years, and the probability that they will begin to leak increases with age. The tanks in the current study are however > 20 years old, thus supporting the likelihood of leakages besides oil spills. When leaks occur, fuel seeps through the soil to the groundwater. The leakage rate of just two drops per second can result in the loss of almost 500 gallons of fuel in one year and can contaminate nearly half a billion gallons of underground water to the point where odour and taste make it unacceptable for drinking [21,63]. However, the soil type, rock type, and other geologic properties such as porosity and permeability of the geologic materials in the locality play significant roles in the leaching rate of the contaminants [16,17,19,46].

4.2. Health risks

Generally, Warri, followed by Asaba, had the most negligible concentrations of the toxicants analyzed. Oghara and Koko had higher concentrations of most toxicants. Notably, the concentration of copper at Koko, followed by Oghara were up to the FMEEnv established limit [46, 48,57].

Although the hazard quotients of all the toxicants analyzed were below the significant level, the most outstanding dermal-associated hazard quotient was in chromium, which occurred at Oghara, in the order of child > male > female. Oghara children also exhibited the highest ingestion hazard quotient in the order of

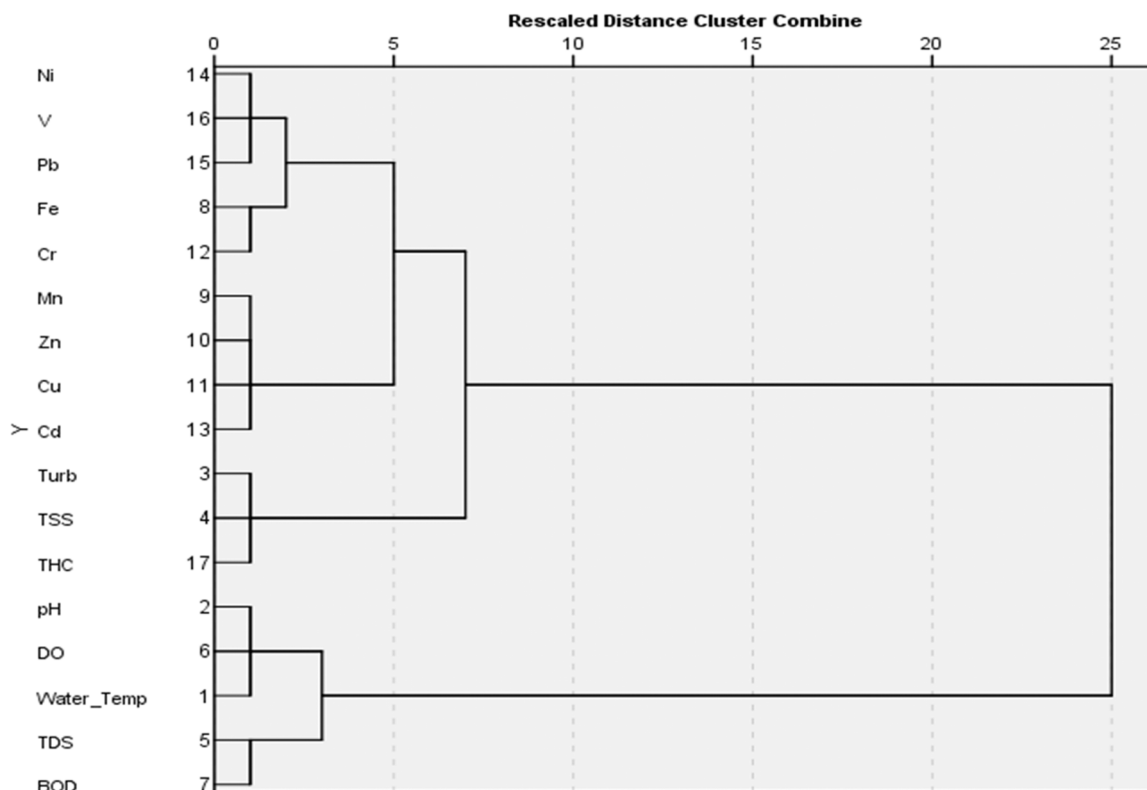


Fig. 10. Dendrogram of parameters in Warri groundwater using Ward linkage.

Table 6
Total variance of parameters in Oghara groundwater.

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total
1	7.287	42.867	42.867	7.287	42.867	42.867	7.049
2	2.979	17.521	60.388	2.979	17.521	60.388	3.461
3	2.866	16.861	77.249	2.866	16.861	77.249	2.856
4	1.575	9.262	86.511	1.575	9.262	86.511	2.094
5	.864	5.081	91.592				
6	.507	2.981	94.574				
7	.411	2.417	96.991				
8	.199	1.170	98.161				
9	.149	.877	99.038				
10	.071	.415	99.454				
11	.063	.372	99.826				
12	.024	.142	99.968				
13	.004	.026	99.994				
14	.001	.005	99.998				
15	.000	.001	100.000				
16	6.315E-5	.000	100.000				
17	1.630E-16	9.587E-16	100.000				

Bold figures indicate parameters with significant values ≥ 1 (Grimm and Yarnold, 2000; Nair et al., 2010).

cadmium > chromium > lead. In the real-life scenario, toxicants are accumulated in the human body through different routes simultaneously, and the resultant effect on the exposed individual is synergistic. Although the combined risk quotients were also not significant, there was an outstanding risk in the average Oghara child compared to the other groups, in the order of chromium, cadmium, and lead. These observations are at variance with the work of Isibor et al. [26], who discovered an order of male > female > children for the dermal, oral, and combined exposures to iron, chromium, and cadmium. The order they detected for lead was male > children > female.

Only in Oghara and Koko towns were cancer risks observed, mainly among the children. All risks recorded were ingestion-associated and THC was the candidate that posed the most threats in the study. THC

posed significant carcinogenic risks to the entire population in Oghara and children in Koko, while chromium posed a carcinogenic threat to the children in Oghara.

There was no significant dermal-associated cancer risk among all the toxicants across the towns (Fig. 6). However, chromium posed a significant oral route cancer risk (ORCR) to the children only in Oghara, the town where THC posed ORCR to the adults and children. Furthermore, in Koko town, THC posed ORCR to the children only (Fig. 7).

4.3. Principal components

In the current study, the extracted component matrix of Oghara groundwater, chromium (0.956) had the highest loading factor and THC

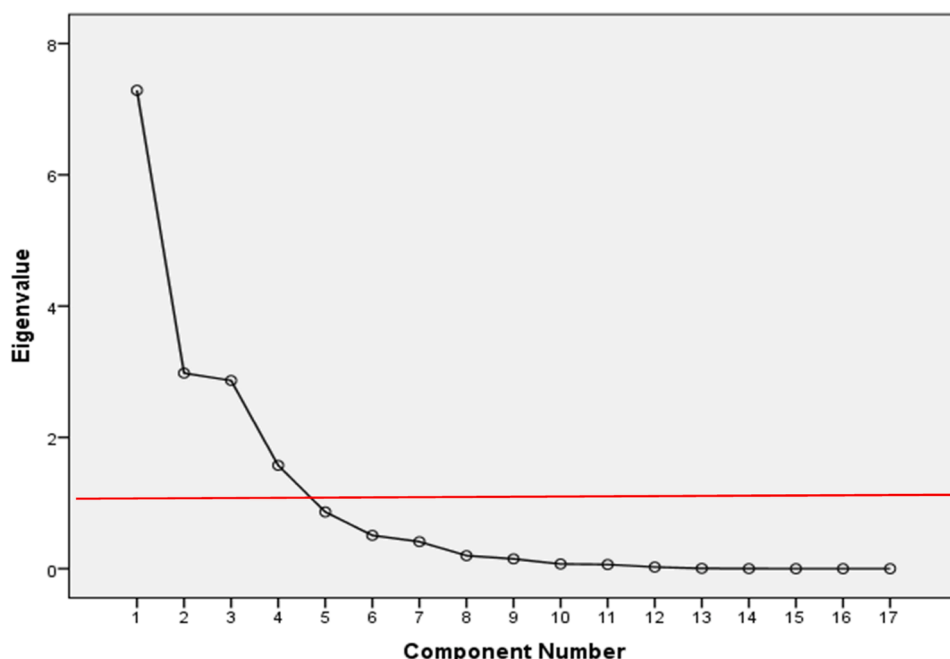


Fig. 11. Scree plot of a component matrix showing significant levels of the Eigenvalues. The redline indicates significant Eigenvalue = 1. (For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)

Table 7

Data of extracted component matrix of Oghara groundwater.

	Component			
	1	2	3	4
Cr	.956	-.217	.202	
Fe	.907			
Pb	.892	-.358		
Cd	.794	-.166	-.522	-.265
Cu	.790	-.273	.403	
Zn	.781	.376	.349	.147
V	.769	-.351	-.146	.135
THC	.754	.351		-.120
Ni	.748		-.167	-.285
TDS	.720		.662	-.118
Mn	.604	.602	-.322	
TSS	.158	.800	.325	.439
BOD		.690	-.598	-.172
Turb	.299	.626	.267	.364
Water_Temp		-.255	.881	-.113
DO	.406	-.472	-.559	.455
pH		-.390	.191	.874

Bold figures indicate parameters with significant loading factors; > 0.71 (Grimm and Yarnold, 2000; Nair et al., 2010).

Table 8

Component Correlation Matrix.

Component	1	2	3	4
1	1.000	.167	-.023	-.047
2	.167	1.000	.034	-.219
3	-.023	.034	1.000	.023
4	-.047	-.219	.023	1.000

(0.754) was also significant among others in component 1, which had the highest initial Eigenvalue of 7.287, percentage variance of 42.867, and rotation sum of square loading of 7.049. In Oghara, the PCA showed a strong cluster among the trace metals and THC analyzed. Notably, the contaminants were uninfluenced by the water temperature and pH in Oghara groundwater. This might be an indication that the area isn't

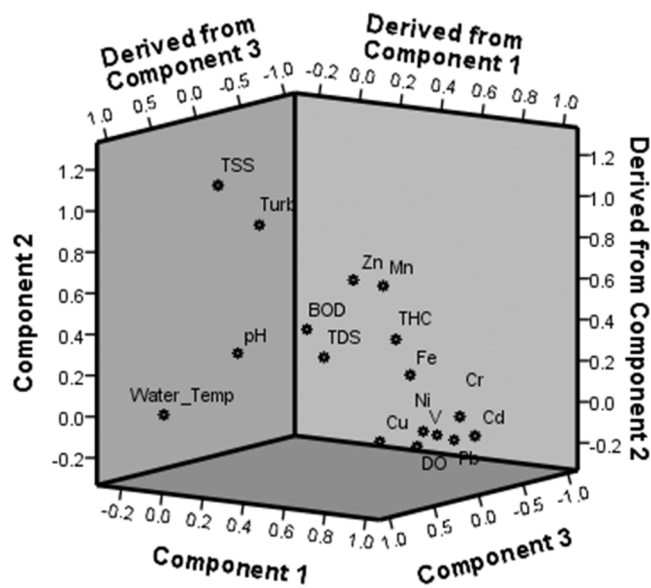


Fig. 12. Scatter plot of PCA in Oghara groundwater.

disturbed by biodegradable organic pollutants which may increase the pH and temperature, thereby influencing the entire physicochemistry. In Warri, the parameters were sparsely distributed, showing the weak influence of the toxicants by the background physicochemical properties, except in DO, and BOD which strongly influenced the concentrations of Fe, Cu, and Cd. The relatively lower concentrations of most of the toxicants in Warri groundwater is attributable to the non-interference of the background physicochemical properties. This might have also played some roles in the overall quality of the water and no determining health risks.

In Koko groundwater, THC (0.881) had a significant loading factor alongside many others in component 1, which had an outstanding Eigenvalue of 8.167, percentage variance of 48.03%, the cumulative percentage of 48.04%, and rotation sum of square loadings of 6.834. The

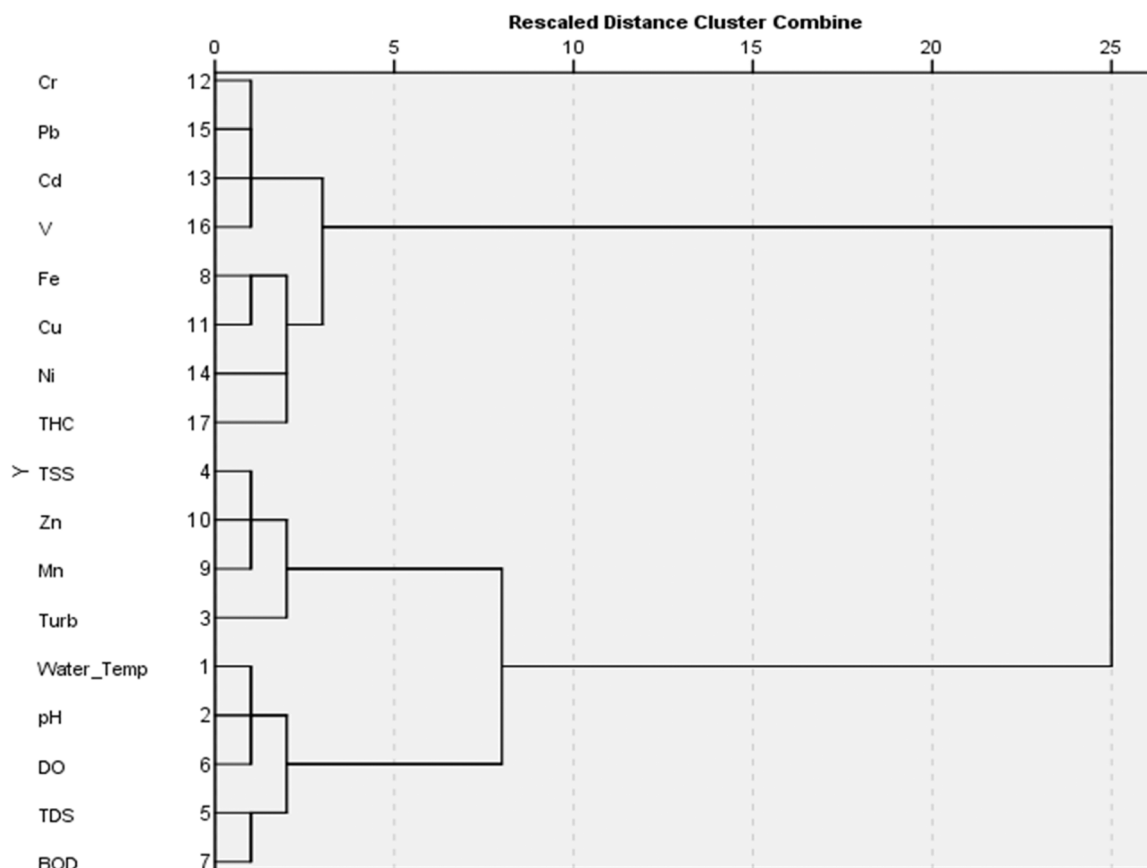


Fig. 13. Dendrogram of parameters in Oghara groundwater using Ward Linkage.

Table 9

Total variance of parameters in Koko groundwater.

Component	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total
1	8.167	48.039	48.039	8.167	48.039	48.039	6.834
2	2.891	17.006	65.045	2.891	17.006	65.045	2.579
3	1.802	10.599	75.644	1.802	10.599	75.644	5.690
4	1.406	8.269	83.913	1.406	8.269	83.913	1.974
5	.984	5.790	89.703				
6	.556	3.273	92.976				
7	.488	2.871	95.847				
8	.332	1.951	97.798				
9	.160	.943	98.741				
10	.114	.672	99.413				
11	.089	.521	99.934				
12	.006	.036	99.970				
13	.005	.029	99.999				
14	.000	.001	100.000				
15	6.522E-16	3.836E-15	100.000				
16	1.174E-16	6.908E-16	100.000				
17	-1.533E-17	-9.016E-17	100.000				

Bold figures indicate significant values ≥ 1 (Grimm and Yarnold, 2000; Nair et al., 2010).

PCA of Koko groundwater showed a strong relationship between THC and other contaminants. This indicates that the contaminants were from a common source, contaminating the water at the same rate. Among the physicochemical parameters, TDS, water temperature, BOD, and DO were the main factors influencing the dynamics of the toxicants in the groundwater. This indicates that there may be a concern for biodegradable organic pollutants in the environment. As expected, TSS and turbidity were strongly linked in the PCA, indicating that the suspended particulates strongly influenced the water’s turbidity of the water. Only pH had no appreciable influence on the other parameters. Hence the

high acidity observed in the groundwater might have played minimal role in determining the concentrations of the toxicants. Conversely, in Asaba groundwater, the toxicants were greatly influenced by the pH, DO, and BOD except for the water temperature; however, there was a strong relationship among the toxicants.

Interestingly, the dendrogram of the physicochemical parameters in Oghara groundwater showed chromium > lead > cadmium ranked highest among all the parameters analyzed. The top rank in dendrogram was buttressed by the extracted component matrix of chromium (0.956) which was the highest. This result, therefore, shows a reliable

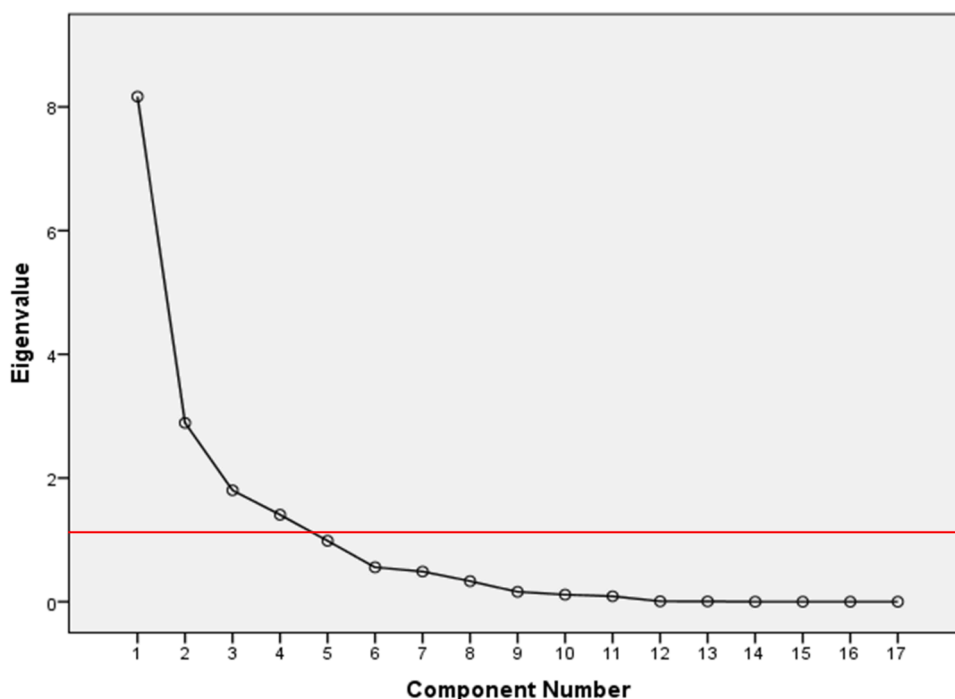


Fig. 14. Scree plot of a component matrix showing significant levels of the Eigenvalues. The redline indicates significant Eigenvalue = 1. (For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)

Table 10

Data of extracted component matrix of Koko groundwater.

	Component			
	1	2	3	4
Cr	.930			
Pb	.913			
Fe	.904	.179	.324	
Cu	.889	-.107	.142	-.123
Cd	.887		-.281	
THC	.881	.233	-.123	
Zn	.814	.144	.408	
Ni	.746	-.205	-.536	
TDS	.737		.525	
V	.734	-.212	-.566	
Mn	.722	.534	.236	
Turb	.106	.810	-.271	-.379
TSS		.804		-.510
pH	-.377	.631	.161	
Water_Temp	.192	-.595	.523	-.287
DO		.572	.183	.666
BOD	.534		-.287	.629

Bold figures indicate parameters with significant loading factors; > 0.71 (Grimm and Yarnold, 2000; Nair et al., 2010).

Table 11

Component Correlation Matrix.

Component	1	2	3	4
1	1.000	-.012	-.404	.025
2	-.012	1.000	.059	.229
3	-.404	.059	1.000	-.018
4	.025	.229	-.018	1.000

corroboration between dendrogram and health risk analysis. This corroborates the results on health hazard which marked out chromium as a significant toxicant posing risks to the children in Oghara. The combination of both shows promising results in managing the environment and public health. The nearest to the top-ranking toxicants is vanadium,

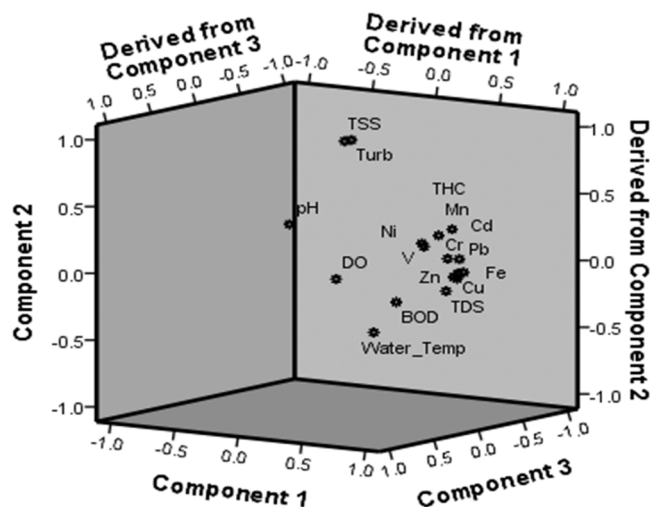


Fig. 15. Scatter plot of PCA in Koko groundwater.

which also deserves prioritized attention to forestall the associated prognosis. Besides their significant extracted component matrices, lead, cadmium, and vanadium formed a robust cluster with chromium, emphasizing their health prognosis. Vanadium concentrations in surface water can range from approximately 0.04 to 220 µg/L depending on geographical location. Experimental exposure of rats to vanadium elicited a decrease in red blood cells, increased blood pressure, and mild neurological effects. Lung cancer has been found in mice exposed to vanadium pentoxide. The International Agency for Research on Cancer (IARC) has identified vanadium as a possible carcinogen to humans [16, 17,19,57].

Although chromium exists in divalent to hexavalent compounds, only the trivalent and hexavalent chromium compounds elicit substantial biological toxicity. In this study, the tank farms are implicated in chromium contamination of the groundwater. In the circulatory system

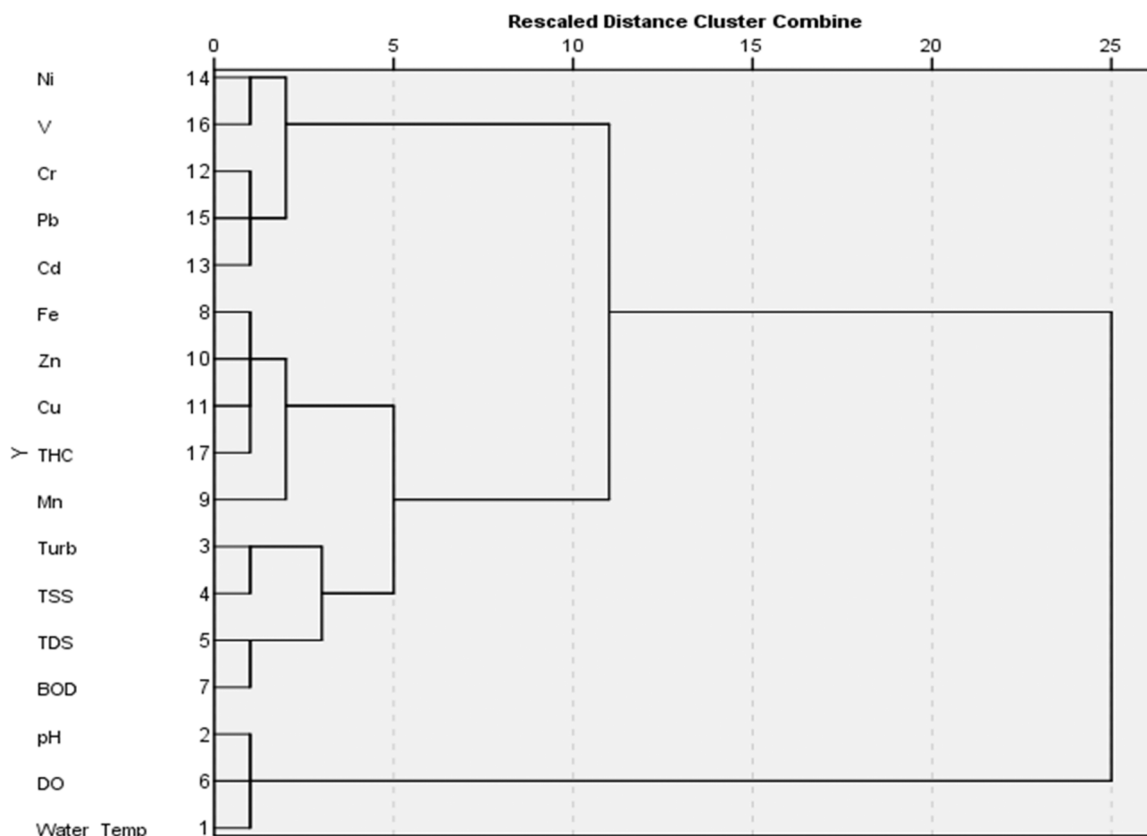


Fig. 16. Dendrogram of parameters in Koko groundwater using Ward Linkage.

Table 12
Total variance of parameters in Asaba groundwater.

Components	Initial Eigenvalues			Extraction Sums of Squared Loadings			Rotation Sums of Squared Loadings
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total
1	6.841	40.242	40.242	6.841	40.242	40.242	3.888
2	2.991	17.597	57.839	2.991	17.597	57.839	3.229
3	2.367	13.922	71.761	2.367	13.922	71.761	2.963
4	1.314	7.727	79.488	1.314	7.727	79.488	2.453
5	1.146	6.743	86.230	1.146	6.743	86.230	2.126
6	.980	5.767	91.998				
7	.517	3.043	95.040				
8	.408	2.399	97.440				
9	.255	1.498	98.938				
10	.126	.741	99.679				
11	.035	.203	99.882				
12	.014	.082	99.965				
13	.005	.031	99.996				
14	.001	.004	100.000				
15	1.737E-16	1.022E-15	100.000				
16	8.380E-17	4.929E-16	100.000				
17	-1.140E-16	-6.705E-16	100.000				

Bold figures indicate significant values ≥ 1 (Grimm and Yarnold, 2000; Nair et al., 2010).

of animals and man, chromium compounds are reduced from hexavalent to trivalent, producing reactive hydroxyl radicals. Mechanism of chromium toxicity includes generation of apoptosis, reactive oxygen species, oxidative stress, and DNA damage. These physiological perturbations may result in dermatitis, nephrotoxicity, malignant tumor, and cancer in children in Oghara.

The entire population in Oghara and the children in Koko towns within the catchment areas of the tank farms are at risk of cancer caused by ingestion of THC in the groundwater. Besides from the carcinogenic and mutagenic tendencies of THC, exposure to the compound may impact the nervous system, cardiovascular system, gastrointestinal tract,

and kidneys. Exposures resulting in seizure and death are usually caused by respiratory failure, and arrhythmias in extreme cases [21,24,46,48, 65].

Metals and THC are known to induce several damages to human organs, even at lower levels of exposure thus classified by the US Environmental Protection Agency (USEPA) and the International Agency for Research on Cancer (IARC) as a human carcinogen. Metals mainly elicit carcinogenesis by inhibiting DNA repair and crosslink with proteins via ROS generation [65]. ROS results in an imbalance in homeostasis between antioxidant and pro-oxidants (metals and hydrocarbons). When the toxicants overwhelm the antioxidant, stress ensues;

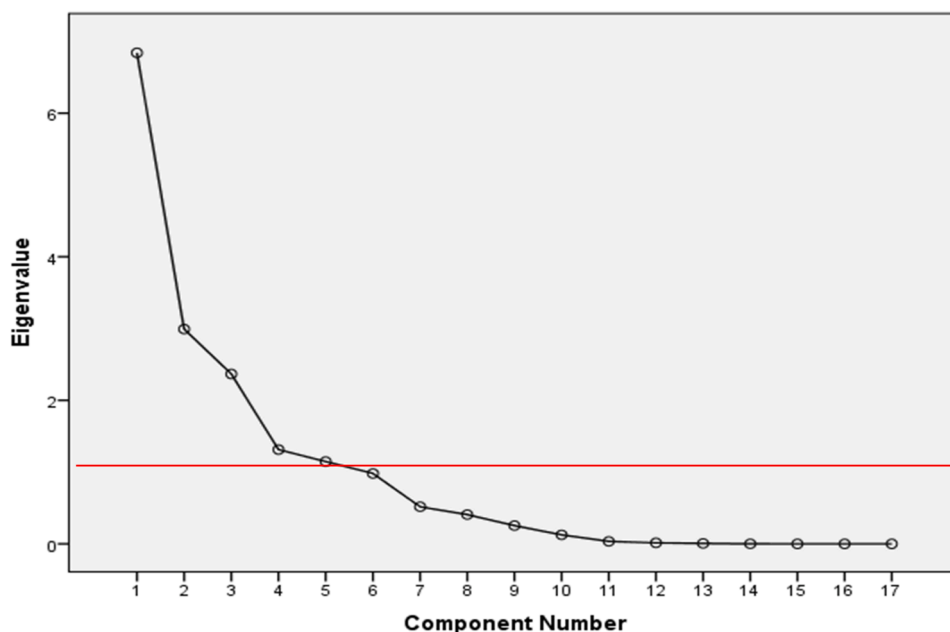


Fig. 17. Scree plot of a component matrix showing significant levels of the Eigenvalues. Redline indicates significant Eigenvalue= 1. (For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)

Table 13
Data of extracted component matrix of Asaba groundwater.

	Component				
	1	2	3	4	5
Cr	.885	-.101	.189	-.123	.288
Ni	.864			.321	.259
V	.815	.104		.453	.168
Zn	.806		-.455		
Fe	.804	-.211	-.396		.159
Cu	.754	-.334	-.358	-.238	.372
Cd	.676		.568	-.117	
pH	-.632	.326	.159	-.491	.311
Pb	.631	-.253	.526		
DO	.493	-.383		-.189	
Turb	-.192	.887			.256
Mn	.585	.655	.222	-.131	-.266
THC	.605	.615	.193	-.252	-.197
TDS	.305	.455	-.734	.221	-.288
BOD	.395	.473	.587	.364	-.256
Water_Temp	-.456	-.359	.249	.586	.142
TSS	-.285	.579	-.414	.140	.587

Bold figures indicate parameters with significant loading factors; > 0.71 (Grimm and Yarnold, 2000; Nair et al., 2010).

characterized by damage to cellular components such as proteins, DNA and lipids [18,53,64].

Metal ions in living organisms can bind with other specific ligand molecules through chelation [15]. Phytochelatins are protein-ligand molecules in plants that chelate metal ions when exposed to metals [14,15,33]. Studies have shown that phytochelatins are also synthesized from glutathione (GSH) by the enzyme phytochelatin synthetase [49, 50], forming GSH oligomers. Metallic ion-bound phytochelatins are transported into the vacuoles and isolated from cellular proteins, thereby reducing metal toxicity [21,35, 38,39,44,67].

5. Conclusion

The study indicated that chromium posed carcinogenic threats to children in Oghara, while THC posed carcinogenic threats to adults and children in Oghara and children alone in Koko. These risks might have

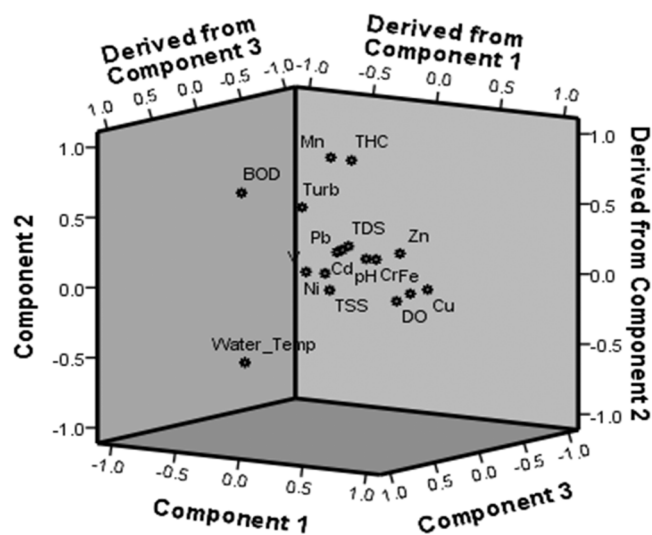


Fig. 18. Scatter plot of PCA in Asaba groundwater.

been mediated through ingestion of the groundwater of Oghara and Koko by the susceptible groups. Of profound attention is the risks chromium poses to the children in Oghara.

Studies on sentinel species such as plankton, benthic, nekton, microorganisms and human subjects are, however required to substantiate the impacts of the tank farms on the groundwater quality of Oghara and Koko and their inhabitants.

CRediT authorship contribution statement

Enuneku Alex Ajeh designed and supervised the study. Odeniyi Olalere Kayode conducted the field and laboratory studies. Isibor Patrick Omoregie analyzed the data, interpreted the results and wrote the manuscript.

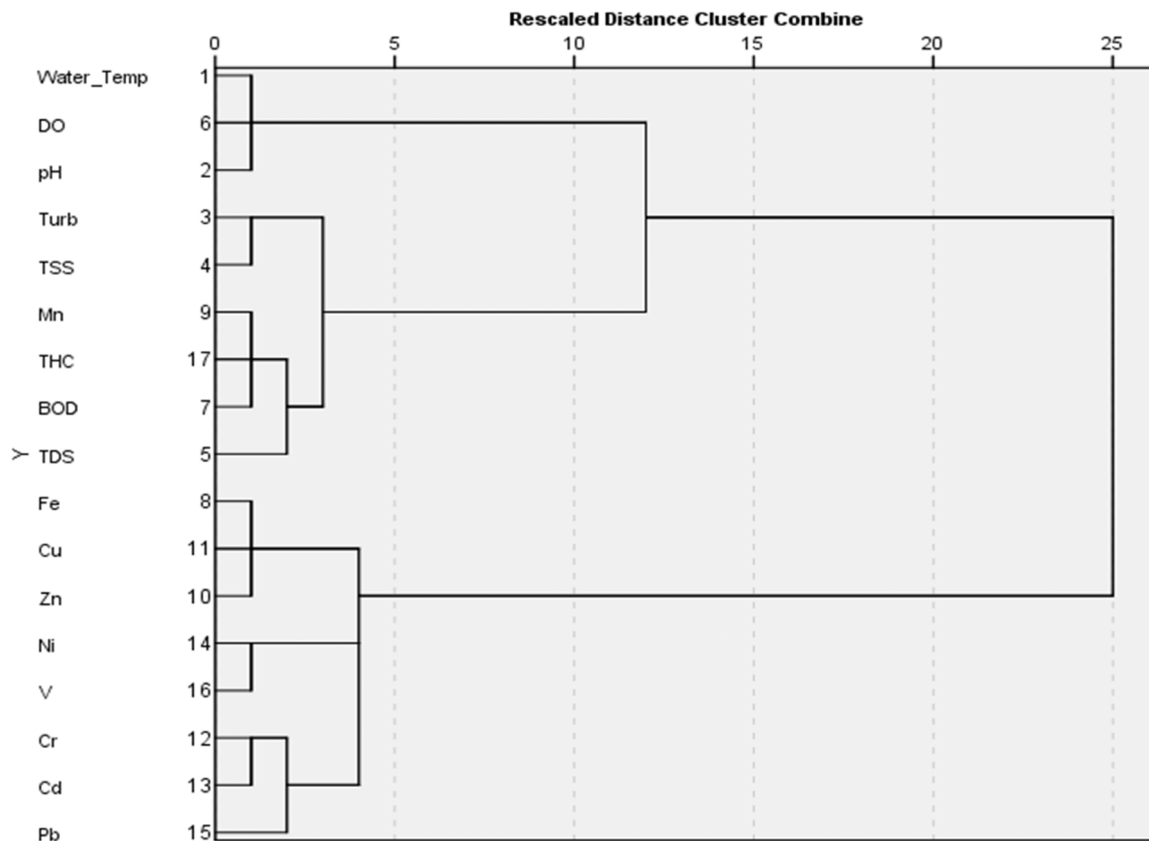


Fig. 19. Dendrogram of parameters in Asaba groundwater using Ward linkage.

Author's statement

I hereby write on behalf of other corresponding Authors to state that this paper has been revised in line with the recommendations required.

The manuscripts has been revised to reduce the similarity index to 10. Verification was done on Grammarly to ascertain this percentage. Thank you.

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.

References

- [1] G.O. Adewuyi , R.A. Olowu , Assessment of oil and grease, total petroleum hydrocarbons and some heavy metals in surface and groundwater within the vicinity of NNPC oil depot in Apata, Ibadan metropolis, Nigeria 13 1 2012.
- [2] Akporido, S.O. , 2008, An assessments of water, sediment and soil pollution arising from crude oil spillages in the vicinity of Esi River, Western Niger Delta. Ph.D. Thesis, Department. Of Chemistry, University of Ibadan.
- [3] S.O. Akporido, S.O. Asagba, Quality characteristics of soil close to the benin river in the vicinity of a lubricating oil producing factory, Koko Nigeria, Int.J. Soil Sci. 8 (2013) 1–16.
- [4] Agency for Toxic Substances and Disease Registry (ATSDR), Toxicological profile for polyaromatic hydrocarbons (PAH) in Goldstein, B.D. et al., (2011) The Gulf Oil Spill, in: New England J. Med., 2010, pp. 1334–1348.
- [5] S. Aggarwal, T. Jilling, S. Doran, I. Ahmad, J.E. Eagen, S. Gu, M. Gillespie, C. J. Albert, D. Ford, J.Y. Oh, R.P. Patel, Matalon S. Phosgene inhalation causes hemolysis and acute lung injury, Toxicol. Lett. 312 (2019) 204–213.
- [6] G.K. Andrews, Regulation of metallothionein gene expression by oxidative stress and metal ions, Biochem. Pharmacol. 59 (2000) 95–104.
- [7] H. Baba, K. Tsuneyama, M. Yazaki, K. Nagatam, T. Minamisaka, T. Tsuda, The liver in itai-itai disease (chronic cadmium poisoning): pathological features and metallothionein expression, Mod. Pathol. 2 6 (2013) 1228–1234.
- [8] O.A. Babatunde, A.O. Oyewale, P.I. Steve, Bioavailable trace elements in soils around Nnpc oil depot Jos, Nigeria, IOSR J. Environ. Science. Toxicol. Food Technol. 8 (1) (2014) 47–56 (IOSR-JESTFT) e-ISSN: 2319-2402,p- ISSN: 2319-2399.
- [9] M. Bilal, H.M.N. Iqbal, An insight into toxicity and human-health-related adverse consequences of cosmeceuticals - a review, Sci. Total Environ. 670 (2019) 555–568.
- [10] K.W. Bock, Aryl hydrocarbon receptor (AHR) functions in NAD+ metabolism, myelopoiesis and obesity, Biochem. Pharmacol. 163 (2019) 128–132.
- [11] E. Casalino, G. Calzaretti, C. Sblano, C. Landriscina, Molecular inhibitory mechanisms of antioxidant enzymes in rat liver and kidney by cadmium, Toxicology 179 (2002) 37–50.
- [12] Casey, B.N., Chirico, P.G., 2013, Topographic and hydrographic GIS datasets for the Afghan Geological Survey and U.S. Geological Survey 2013 mineral areas of interest: U.S. Geological Survey Open-File Report 2013–1124, 16 p.
- [13] S.K. Chakrabarti, C. Bai, K.S. Subramanian, DNA-protein crosslinks induced by nickel compounds in isolated rat lymphocytes: role of reactive oxygen species and specific amino acids, Toxicol. Appl. Pharmacol. 170 (2001) 153–165.
- [14] C.S. Cobbett, Phytochelatin biosynthesis and function in heavy metal detoxification, Curr. Opin. Plant Biol. 3 (2000) 211–216.
- [15] C. Cobbet, P. Goldsbrough, Phytochelatin and metallothioneins: roles in heavy metal detoxification and homeostasis, Annu. Rev. Plant Biol. 53 (2002) 159–182.
- [16] Egborge, A.B.M., Onwudinjo, C.C., Chigbu, P.C. ,1994 , Cladocera of Coastal Rivers of Western Nigeria. Department of Zoology, University of Benin, Nigeria; School of Fisheries, University of Washington, Seattle, WA 98195, USA. Hydrologia. 272, 39–46.
- [17] Environmental Research Institute, 1999, Analysis of Extractable Total Petroleum Hydrocarbons Using Methylene Chloride: Gas Chromatograph/Flame Ionization Detection, University of Connecticut.
- [18] N. Ercal, H. Gurer-Orhan, N. Aykin-Burns, Toxic metals and oxidative stress part 1: mechanism involved in metal-induced oxidative damage, Curr. Top Med. Chem. 1 (2001) 529–539.
- [19] Federal Environmental Protection Agency (FEPA). Guidelines and Standards for Environmental pollution control in Nigeria. Pp 420 (2003).
- [20] Glowacka, Malgorzata, 2005, Soil and groundwater contamination with gasoline and diesel oil: assessment of subsurface hydrocarbon contamination resulting from a fuel release from an underground storage tank in Vanstad, Skåne, Sweden. Dissertations in Geology at Lund University.
- [21] N. Harrison, Inorganic contaminants in food (Ltd), in: D.H. Watson (Ed.), Food Chemical Safety Contaminants, first ed., Woodhead Publishing, Cambridge, 2001, pp. 148–168.
- [22] M.C. Henson, P.J. Chedrese, Endocrine disruption by cadmium, a common environmental toxicant with paradoxical effects on reproduction, Exp. Biol. Med. 229 (2004) 383–392.

- [23] T. Huang, Q. Guo, H. Tian, X. Mao, Z. Ding, G. Zhang, J. Li, J. Ma, H. Gao, Assessing spatial distribution, sources, and human health risk of organochlorine pesticide residues in the soils of arid and semiarid areas of northwest China, *Environ. Sci. Pollut. Res.* 21 (2014) 6124–6135.
- [24] International Agency for Research on Cancer (IARC), 2012, Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Humans, Vol. 32, Polynuclear Aromatic Compounds, Part 1, Chemical, Environmental and Experimental Data, Lyon. 239–245pp.
- [25] P.O. Isibor, Heavy metals, nutrients, total hydrocarbons and Zooplankton community structure of Osse River, Edo State, Nigeria, *Jordan J. Biol. Sci.* 10 (2) (2017) 109–116.
- [26] Isibor, P.O., Imoobe, T.O. T., Enuneku, A.A., Akinduti, P.A., Dedeke, G., Adagunodo, T.A., Obafemi, Y.D., 2020, Principal Components and Hierarchical Cluster Analyses of Trace Metals and Total Hydrocarbons in Gills, Intestines and Muscles of *Clarias gariepinus* (Burchell, 1822). *Scientific Report*, (2020) 10:5180.
- [27] H. Itoh, M. Iwasaki, N. Sawada, R. Takachi, Y. Kasuga, S. Yokoyama, Dietary cadmium intake and breast cancer risk in Japanese women: a case-control study, *Int. J. Hyg. Environ. Health* 217 (2014) 70–77.
- [28] S. Jahan, M. Khan, S. Ahmed, H. Ullah, Comparative analysis of antioxidants against cadmium induced reproductive toxicity in adult male rats, *Syst. Biol. Reprod. Med.* 60 (2014) 28–34.
- [29] K.A. James, J.R. Meliker, Environmental cadmium exposure and osteoporosis: a review, *Int. J. Public Health* 58 (2013) 737–745.
- [30] C. Kamunda, M. Mathuthu, M. Madhuku, Health risk assessment of heavy metals in soils from witwatersrand gold mining basin, South Africa, *Int. J. Environ. Res. Public Health* 13 (2016) 663.
- [31] H.L. Kim, Y.R. Seo, Molecular and genomic approach for understanding the gene-environment interaction between Nrf2 deficiency and carcinogenic nickel-induced DNA damage, *Oncol. Rep.* 28 (2012) 1959–1967.
- [32] H.S. Kim, Y.J. Kim, Y.R. Seo, An overview of carcinogenic heavy metal: molecular toxicity mechanism and prevention, *J. Cancer Prevent.* 20 (4) (2015) 232–240.
- [33] A.M. Kinnerly, The role of phytochelate in plant growth and productivity, *Plant Growth Regul.* 12 (1993) 207–218.
- [34] J. Kotaš, Z. Stasicka, Chromium occurrence in the environment and methods of its speciation, *Environ. Pollut.* 107 (2000) 263–283.
- [35] X. Lu, X. Zhang, L.Y. Li, H. Chen, Assessment of metals pollution and health risk in dust from nursery schools in Xi'an, China, *Environ. Res.* 128 (2010) 27–34.
- [36] S. Lynn, F.H. Yew, K.S. Chen, K.Y. Jan, Reactive oxygen species are involved in nickel inhibition of DNA repair, *Environ. Mol. Mutagen.* 29 (1997) 208–216.
- [37] A.G. Marshall, R.P. Rodgers, *Petroleomics: Chemistry of the underworld* Proceedings of the National Academy of Sciences of the USA 105 2008 18090 18095 doi: 10.1073/pnas.0805069105.
- [38] Matsumoto, N., 2009, Groundwater Contamination Prevention and Cleanup in the Central and West Coast Basins. WRD Technical Bulletin Volume 18.
- [39] A.D. McNaught, A. Wilkinson, *Compendium of Chemical Terminology*, Blackwell Science, Oxford, 1997.
- [40] A. Mudhoo, S.K. Sharma, V.K. Garg, C.-H. Tseng, Arsenic: an overview of applications, health, and environmental concerns and removal processes. *Critical reviews in Environ. Sci. Technol.* 41 (2011) 435–519.
- [41] NEPAC, 2014, Technical Guidance for Risk Assessment to Contaminated Sites; HJ25.3-2014; NEPAC: Beijing, China.
- [42] National Research Council (NRC), *Risk Assessment in the Federal Government: Managing the Process*, National Academy Press, Washington, DC, 1983.
- [43] K. Nogawa, E. Kobayashi, Y. Okubo, Y. Suwazono, Environmental cadmium exposure, adverse effects and preventive measures in Japan, *Biomaterials* 17 (2004) 581–587.
- [44] R. Olawoyin, S.A. Oyewole, R.L. Grayson, Potential risk effect from elevated levels of soil heavy metals on human health in the Niger delta, *Ecotoxicol. Environ. Safe.* 85 (2012) 120–130.
- [45] J.L. Peters, T.S. Perlstein, M.J. Perry, E. McNeely, J. Weuve, Cadmium exposure in association with history of stroke and heart failure, *Environm. Res.* 110 (2) (2010) 199–206.
- [46] QGIS Development Team, 2019, QGIS Geographic Information System. Open Source Geospatial Foundation Project. URL: <https://qgis.org/en/site/forusers/download.html#>.
- [47] C. Qu, Q. Shihua, Y. Dan, H. Huanfang, Z. Jiaquan, C. Wei, K.Y. Habtom, H. S. Edward, Y. Junhua, X. Xinli, Risk assessment and influence factors of organochlorine pesticides (OCPs) in agricultural soils of the hill region: a case study from Ningde, southeast China, *J. Geochem. Explorat.* (2014).
- [48] D.V. Rasmussen, Characterization of oil spill by capillary column gas chromatography, *Anal. Chem.* 48 (11) (1976) 1536–1566.
- [49] W.E. Rauser, Phytochelatin and related peptides, *Struct. Biosyn. Function Plant Physiol.* 109 (1995) 1141–1149.
- [50] W.E. Rauser, Structure and function of metal chelators produced by plants: the case for organic acids, amino acids, phytin, and metallothioneins, *Cell Biochem. Biophys.* 31 (1999) 19–48.
- [51] R. Rubin, D.S. Strayer, *Environmental and Nutritional pathology. Rubins Pathology; Clinicopathologic Foundations of Medicine*, fifth ed., Lipincot Williams & Wilkins, 2008.
- [52] Z.A. Shaikh, T.T. Vu, K. Zaman, Oxidative stress as a mechanism of chronic cadmium-induced hepatotoxicity and renal toxicity and protection by antioxidants, *Toxicol. Appl. Pharmacol.* 154 (1999) 256–263.
- [53] H. Sies, Oxidative stress: oxidants and antioxidants, *Exp. Physiol.* 82 (1997) 291–295.
- [54] B.R. Singh, S.K. Gupta, H. Azaizah, S. Shilev, D. Sudre, W.Y. Song, M. Mench, Safety of food crops on land contaminated with trace elements, *J. Sci. Food Agric.* 91 (8) (2011) 1349–1366.
- [55] M. Songbo, H. Lang, C. Xinyong, X. Bin, Z. Ping, S. Liang, Oxidative stress injury in doxorubicin-induced cardiotoxicity, *Toxicol. Lett.* 307 (2019) 41–48.
- [56] S. Takebayashi, S. Jimi, M. Segawa, Y. Kiyoshi, Cadmium induces osteomalacia mediated by proximal tubular atrophy and disturbances of phosphate reabsorption. A study of 11 autopsies, *Pathol. Res. Pract.* 196 (2000) 653–663.
- [57] B.V. Tangahu, S.R. Sheikh Abdullah, H. Basri, M. Idris, N. Anuar, M. Mukhlisin, A review on heavy metals (As, Pb, and Hg) uptake by plants through phytoremediation, *Int. J. Chem. Eng.* (2011) (2011) 1–31.
- [58] P.B. Tchounwou, C.G. Yedjou, A.K. Patlolla, D.J. Sutton, Heavy metals toxicity and the environment, *Mole. Clin. Environ. Toxicol.* 101 (2012) 133–164, <https://doi.org/10.1007/978-3-7643-8340-4>.
- [59] S.V. Torti, F.M. Torti, Iron and cancer: more ore to be mined, *Nat. Rev. Cancer* 13 (2013) 342–355.
- [60] US EPA (US Environmental Protection Agency), 2010, Risk-Based Concentration Table. United States Environmental Protection Agency. Available at: (<http://www.epa.gov/reg3hwmd/risk/human/index.htm>).
- [61] US EPA (US Environmental Protection Agency), 2011, Recommended Use of BW3/4 as the Default Method in Derivation of the Oral Reference Dose. EPA/100/R11/001. Office of the Science Advisor. (<http://www.epa.gov/raf/publications/pdfs/recommended-use-of-bw34.pdf>).
- [62] USDOE (United States Department of Energy), 2011, U.S. Department of Energy's Oak Ridge Operations Office (ORO). The Risk Assessment Information System (RAIS).
- [63] S.A. Uzoekwe, F.A. Oghosanine, The effect of refinery and petrochemical effluent on water quality of Ubeji creek Warri, Southern Nigeria, *Ethiopian J. Environ. Studies Manag.* 4 (2) (2011) 107–116.
- [64] S. Vertuani, A. Augusti, S. Manfredini, The antioxidants and proantioxidants network: an overview, *Curr. Pharm. Des.* 10 (2004) 1677–1694.
- [65] S. Wang, K.A. Meckling, M.F. Macrone, Y. Kakuda, R. Tsao, Can Phytochemical antioxidant rich foods act as anti-cancer agent? *Food Res. Int.* 44 (2011) 2545–2554.
- [66] A.L. Wani, A. Ara, J.A. Usmani, Lead toxicity: a review, *Interdiscip. Toxicol.* 8 (2) (2015) 55–64.
- [67] World Health Organization (WHO), 2008, Cadmium in Drinking-water. Background document for development of WHO Guidelines for Drinking-water Quality.