

Vol. 5 No. 1 (2024) 40-51 https://publisher.uthm.edu.my/ojs/index.php/j-sunr

Environmental Assessment of Heavy Metal Pollution around Industrial Area in Southwestern, Nigeria

Kehinde Olojoku Ibrahim¹*, Muyiwa Michael Orosun², Megan Welman Purchase³, Mumeen Adebayo Yusuf¹

- ¹ Department of Geology and Mineral Sciences, University of Ilorin, Ilorin, NIGERIA
- ² Department of Physics, University of Ilorin, Ilorin, NIGERIA
- ³ Department of Geology, University of the Free State, SOUTH AFRICA

*Corresponding Author: ibrahim.ko@unilorin.edu.ng DOI: https://doi.org/10.30880/jsunr.2024.05.01.005

Article Info

Abstract

Received: 25 November 2023 Accepted: 26 June 2024 Available online: 30 June 2024

Keywords

Carcinogenic, non-carcinogenic, heavy metals, health, environment

This study investigated heavy metal contamination around an industrial district in Obajana, Southwest Nigeria. The study region lies between latitudes 7°54'N to 7°56'N and longitudes 6°24'E to 6°27'E. Thirty samples each for groundwater and soil and twelve plant samples were collected from the study area. All samples were collected in triplicate. The physical and chemical parameters of the groundwater, soil, and plant samples were measured. The average pH level of the groundwater samples is 7.2 which falls within the Nigerian Standards for Drinking Water Quality (NSDWQ). The ranges of the other physical parameters such as electrical conductivity (EC), total dissolved solids (TDS) and total hardness (TH) are also within the acceptable limits. The mean concentrations of heavy metals in groundwater samples for Mn (0.020 mg/L), Zn (0.010 mg/L), Ni (0.010 mg/L), Cr (0.130 mg/L), Cu (0.020 mg/L), and Fe (0.090 mg/L) are within the allowable limit, with the exception of Pb (0.090 mg/L) that is above the recommended level. According to the index of geo-accumulation (Igeo), the soil and plant samples are not polluted with respect to the heavy metals tested. The analysis of the human risk assessment reveals that the values for the carcinogenic risk are within acceptable bounds; however, the values for the non-carcinogenic risk are substantially above the acceptable bounds. This demonstrates that non-carcinogenic health impacts are a threat to the broader population. This study suggests continuous monitoring of groundwater, soil, and plant in the study area.

1. Introduction

Man's capacity to harness natural energy resources to improve the quality of life through economically driven mechanised manufacturing has been linked to industrialisation and economic progress. Both developed and emerging nations have experienced socioeconomic progress as a result of industrialisation, which will continue to foster economic growth and job creation. Although industrialisation is regarded as the cornerstone of all socioeconomic growth, it causes some issues that affect the environment [2, 3]. High production volumes are always accompanied by a significant amount of garbage, and this waste can have a severe influence on the environment.

Industrial effluents are liquid wastewater that is either treated, untreated, or partially treated before being released from industrial operations into bodies of surface water, groundwater, and soil [4]. If not handled properly, these industrial effluents will either directly or indirectly pollute the soil, plants, and aquifer system [3, 5] and generate some heavy metals that may have adverse effects on human health, distort plant growth, damage soil, and destabilise ecosystems. Additionally, untreated wastes that companies release into the groundwater aquifer contaminate the water [3, 5]. Evaluation of heavy metals near industrial sites has recently become a crucial topic to be investigated in order to protect our environment. This research region focuses on Dangote cement factory, the largest in Africa which was made possible by the abundance of marble as raw material for cement production.

A marble deposit is thought to exist in the research region at a depth of between 30 and 60 m, weighing approximately 450,000,000 tons [6]. The production of cement and marble are two of the main businesses that produce wastes in the study area. The mining, processing, and polishing stage cover over 70% of the marble production processes which brings upon a number of environmental implications. For instance, the sawing or cutting phase produces noise and dust, and the cutting and polishing stages involve the use of chemicals that may contaminate the water [7]. Additionally, with the growth of cement factories, dust emissions from the cement sector have dangerously increased. This type of industry releases many pollutants in its industrial discharge, which have a direct impact on the environment [8]. The composition of the organic and inorganic materials in cement industry effluents, including potassium, sodium, calcium, magnesium, chloride, sulphate, and carbonate, varies with time. When the effluent eventually mixes with water, it may also cause consequential changes in the level of the heavy metals (Zn, Mn, Pb, Cr, Cu, Fe, Ni, Cd) in water, soil, and plant [9]. Additionally, the ecosystem deteriorates when certain metals are present in excessive amounts.

Numerous research has suggested environmental protection regulations in response to worries regarding environmental preservation and the adverse effects of the industry on human health. Marble as a raw material for cement production in the study area has been thoroughly investigated in terms of its mineralogy and industrial applications [10]; however, previous studies have not reported any implications regarding the discharge of untreated industrial waste in the study area. Thus, this study was carried out to investigate heavy metal contamination around the industrial areas in Southwest Nigeria.

2. Study Location and Geology

The study area is a small community in Obajana, Southwest Nigeria and lies between latitudes 7°54'N to 7°56'N and longitudes 6°24'E to 6°27'E. It belongs to the Local Government Area of Lokoja with two landforms: dome-shaped residual hills and river valley. The study area consists of metasediments and folded gneisses underlain by granite–gneiss, quartzite, quartz–mica schist, phyllites and marble. Obajana Cement Plc (OCP), now known as Dangote Cement Plc, was incorporated by the Kogi State Government in 1992 [11]. Majority of the activities here are owned by this company.



Fig. 1 Geological map of Nigeria showing the study area [12]



3. Materials and Methods

Thirty samples each of groundwater and soil were taken from 10 randomly chosen hand-dug wells, while 12 plant samples for cassava leaves, cassava tubers, sugarcane, and mango leaves were taken from 4 randomly chosen locations. All samples were collected in triplicate at each sampling points in the middle of January 2023. Groundwater samples were taken using 1 L polyethylene bottles from hand-dug wells in unconfined aquifers that ranged in depth from 8 to 12 m. The physical characteristics of groundwater samples were assessed on-site using a portable meter (MI 806, Martini Instruments). Before collection of water samples, the water from hand-dug wells was left to flow for around 2 min while the containers were carefully cleansed and rinsed [13]. The water samples were analysed using atomic absorption spectrophotometry (AAS) at the Central Research Laboratory, University of Ilorin, within 24 h of collection. In this study, the means for the datasets were calculated using the descriptive statistics approach for the health risk assessment.

Soil samples were collected between depth of 3 to 5 cm. Plants growing in the soils were gathered, including sugarcane leaves (*Saccharum officinarum*), mango leaves (*Mangifera indica*), immature cassava leaves (*Manihot esculenta*) that are utilised as vegetables, and cassava tubers. A vortex stirrer was used to combine 25 mL of 0.1% HNO3, which was then transferred to a 50 mL centrifuge tube, sealed, and centrifuged for 15 m at 500 rpm. The digestion process was monitored for 20 minutes under these parameters: 180 °C for 120 minutes and 200 °C for 30 minutes. Once the block had been digested, the tubes were taken out and left to cool at ambient temperature. A decanted sample of 10 mL of the digested solution was used for AAS. Heavy metal detection thresholds are 0.03 mg/L (Mn), 0.08 mg/L (Pb), 0.7 mg/L (Zn), and 0.005 mg/L (Cu). The percentage recovery was unknown since the samples were not spiked and their initial concentrations were not established prior to the laboratory analysis.



Fig. 2 Location map of study area showing sampled points

3.1 Metal Pollution Index (MPI)

The metal pollution index (MPI) measures the influence of metallic elements on the overall water quality [14] and assesses the specific components that could affect the water quality. A higher concentration of a metal compared to its maximum allowable limit indicates lower quality [15]. The MPI is calculated using Eq. (1):



$$MPI = \sum_{i=1}^{n} \left(\frac{C_i}{MACi}\right) \tag{1}$$

where MACi is the maximum permissible concentration and Ci is the mean concentration. Pollution levels are categorised into 5 groups based on the MPI value; value less than 0.01 means very lightly polluted; value between 0.01 and 1.0 means lightly polluted; value between 1.0 and 5.0 means moderately polluted; value between 5.0 and 10.0 means highly polluted; and value greater than 10.0 means very highly polluted.

3.2 Index of Geo-Accumulation (Igeo)

Metal concentration in soil, plants, sediment, and rock is measured using the index of geo-accumulation (Igeo) [16]. The index of geo-accumulation is calculated using Eq. (2):

$$Igeo = ln\left(\frac{Cm}{1.5}\right) * Bm \tag{2}$$

where Cm is the average concentration of metal m, Bm refers to the background value of metal m, and 1.5 is the factor for potential variation in the background value that could result from lithologic differences. Bm is based on average crustal abundance with similar geological formation. A value of Igeo below 1 is unpolluted and 1.0 to 1.99 is polluted. Between 2.0 to 2.99 is lightly polluted while 3.0 to 3.99 is moderately polluted and 4.0 to 5.0 is highly polluted.

3.3 Health Risk Assessment of the Heavy Metals

A risk index was used to express the link between toxic chemicals and their harm to human health using the risk assessment models developed by the USEPA [17–21]. The heavy metal toxicological profiles used in the health risk assessment were referred to the Toxicological Profiles from the United States Agency for Toxic Substances and Disease Registry [18, 22, 23], Risk Assessment Information System (RAIS), and Integrated Risk Information System (IRIS) [17]. In the current study, the chronic daily dose (CDD) of each heavy metal through oral and dermal absorption pathways was determined, which served as the starting point for the health risk assessment of the heavy metals (Pb, Fe, Mn, Zn, Ni, Cr, & Cu).

The CDD (mg/L/day) for oral and dermal pathways were estimated using Eqs. (3) and (4), respectively [22].

$$CDD_{oral-water} = \frac{Cw \times IngRw \times EF \times ED}{BW \times AT} \frac{Cw \times IngRw \times EF \times ED}{BW \times AT}$$
(3)

$$CDD_{derm-water} = \frac{Cw \times SA \times KP \times ABS \times ET \times EF \times ED}{BW \times AT} = \frac{Cw \times SA \times KP \times ABS \times ET \times EF \times ED}{BW \times AT}$$
(4)

where Cw is the concentration of heavy metals in the sample and BW is body mass (Standard used: 70 kg). The lifetime exposure duration (ED) is 30 years for hazards that are not carcinogenic and 55 years on average for dangers that are. AT is the time during which the dose is averaged (ED × 365 days for non-carcinogenic risk and Lifetime (55 years) × 365 days for carcinogenic risk), and EF is the exposure frequency (350 days/year). IngRw is the ingestion rate of the drinking water (2 L/day). Dermal permeability constant, KP, is 0.0001; exposed skin surface area, SA, is 18,000 cm2; exposure duration, ET, is 0.58 h/event; and dermal absorption factor, ABS, is 0.001 [22, 17, 19, 23].

3.3.1 The Carcinogenic and Non-Carcinogenic Risk Assessment

The ratio of the calculated CDD to reference dose (RfD) of the selected heavy metals, also known as target hazard quotient (HQ), is usually employed to highlight the level of the non-carcinogenic risks [22, 24, 25]. HQ was calculated by using Eq. (5) [19]:

$$HQ = \frac{CDD}{RfD} \frac{CDD}{RfD}$$
(5)

For Pb, Mn, Zn, Ni, Cr, and Cu, the corresponding doses are 0.0035, 0.046, 0.3, 0.02, 0.003, and 0.04 mg/L/day for the oral pathway and 5.25×10⁻⁴, 0.00184, 0.06, 0.0054, 6×10⁻⁵, and 0.0120 mg/L/day for the dermal pathway, respectively. The chance of hazardous consequences is high if the estimated value of HQ is larger than 1, and the probability is lower if the estimated value of HQ is less than 1 [22]. The accumulation of each heavy metal's HQ was evaluated using Eq. (6) to determine the hazard index (HI) [22, 25]:



$$HI = \sum HQ \sum HQ$$
 (6)

Cr, Ni, and Pb are known human carcinogens with carcinogenic oral slope factors of 0.5, 0.840, and 0.0085 mg/L/day respectively, according to the toxicological profiles and risk methodology [19, 26, 27]. The cancer risk appraisal offers a measure of the likelihood that a person would get cancer as a result of exposure to the carcinogenic substances in water samples over the course of an estimated lifespan. Equation (7) was used to assess the incremental lifetime cancer risk (ILCR), which represents the magnitude of the carcinogenic risk [28].

$$ILCR = CDD \times SF$$
(7)

where CDD (mg/L/day) and SF (mg/L/day)⁻¹ represent the average daily doses of the heavy metals and the oral slope factor for cancer, respectively. The appropriate range for ILCR is between 1×10^{-4} and 1×10^{-6} , with values above 1×10^{-4} deemed high because they may present a greater cancer threat and values below 1×10^{-6} assumed to not present any cancer risk to the general population. The gastrointestinal absorption factor (ABS_{gi}), a pertinent modification factor that makes use of the oral slope. The slope factor for the cutaneous exposure pathway was calculated using the oral slope factor. The adjustment factor is based on a chemical's gastrointestinal tract absorption. The values of ABS_{gi} for various hazardous chemicals were obtained from a USEPA manual [17]. The dermal exposure pathway's carcinogenic slope factor was calculated using Eq. (8) [17, 29]:

$$CSF_{dermal} = \frac{CSF_{oral}}{ABS_{gi}} SF_{dermal} = \frac{CSF_{oral}}{ABS_{gi}}$$
(8)

where CSForal is the cancer slope factor for the oral pathway (mg/kg/day) $^{-1}$, CSFdermal is the slope factor for dermal pathway (mg/kg/day) $^{-1}$, and ABS_{gi} is the gastrointestinal absorption factor (Pb = 1.00, Cr = 0.013, and Ni = 0.04) [30, 29].

4. Discussion of Results

4.1 Heavy Metals in Groundwater

The physicochemical parameters and metal pollution index of groundwater are summarised in Table 1 and Table 2, respectively.

Parameter	Minimum	Maximum	Mean	Maximum allowable limit [13]
pH	6.700	7.800	7.200	6.500-8.500
EC (µS/cm)	115.000	457.000	213.000	1200.000
TDS (mg/L)	12.000	232.000	93.000	1500.000
TH (mg/L)	39.000	124.000	67.000	500.000
Lead (Pb)	0.010	0.100	0.090	0.010
Iron (Fe)	0.030	0.210	0.090	0.300
Manganese (Mn)	0.010	0.070	0.020	0.200
Zinc (Zn)	0.010	0.020	0.010	3.000
Nickel (Ni)	0.010	0.020	0.010	0.020
Chromium (Cr)	0.010	0.020	0.010	0.050
Copper (Cu)	0.010	0.060	0.020	1.000

Table 1 Statistical summary of physicochemical parameters of groundwater

The mean concentrations of physicochemical parameters in groundwater samples are within standards of NSDWQ (Table 1). The average pH value is 7.2 and also falls within the acceptable limit [13]. The electrical conductivity (EC), total dissolved solids (TDS), and total hardness (TH) have mean values of 213 μ S/cm, 93 mg/L, and 67 mg/L, respectively, all below the NSDWQ acceptable limits. The average lead (Pb) concentration in groundwater is 0.090 mg/L. This value is higher than NSDWQ's allowable value of 0.010 mg/L. This may be due to the use of coal as a secondary energy source during the production of cement (approximately 35%), after natural gas (57%). High lead concentration beyond the permissible threshold may be due to the untreated industrial effluent discharge in the study area. The high lead concentrations around industrial locations have also been attributed to fossil fuel combustion and power plant emissions in previous studies [31–33], supporting the possibility that lead comes from untreated industrial waste discharge in the study area. Lead is a carcinogen that



damages the kidney, cardiovascular system, and reproductive system in humans [34]. In children under the age of 6, lead can cause hearing loss and hyperactivity [31].

The average iron (Fe) concentration is 0.090 mg/L, which is lower than the permissible value of 0.300 mg/L. Iron is a necessary nutrient for the process by which cells produce energy. High iron content may cause the water to have poor taste and colour. Additionally, high iron concentration might accelerate the generation of free radicals, which are linked to aging and degenerative diseases [34]. Manganese (Mn) has a mean concentration of 0.020 mg/L, which is below the standard limit of 0.200 mg/L. Animals and plants both require manganese. It is also used to create items like batteries, glass, and pyrotechnics. Industrial wastewater decomposition and subsequent leaching are potential sources of manganese in groundwater. The average zinc concentration is 0.010 mg/L, which is less than the permitted maximum of 3.000 mg/L. One of the most prevalent elements in the crust of the earth is zinc. It can be found in food as well as in the soil, water, and air. Zinc can be used as a coating to stop rust. Zinc compounds can be used to create rubber, paint, and dyes. However, high zinc intake might cause intestinal haemorrhage and muscular pain [34]. The average concentration of nickel is 0.010 mg/L, which is less than the permitted limit of 0.020 mg/L. Nickel is a highly common element in nature and is typically found as oxides or sulphides. The average concentration of chromium (Cr) is 0.010 mg/L, which is below the acceptable value of 0.050 mg/L. Chromium occurs as a natural element and in volcanic gases. It is helpful in the production of other alloys and bricks. Chromium poisoning leads to skin ulcers, seizures, kidney, and liver damage [8]. The average concentration of copper (Cu) is 0.020 mg/L, which is below the permissible level of 1.000 mg/L. Despite being a heavy metal that is harmful if it accumulates, copper is necessary for life. High copper content in drinking water may lead to gastrointestinal problems in people. The high concentrations in some of the heavy metals, particularly lead, could be from the release of untreated industrial effluents brought by use of coal as a secondary energy source and the interaction of these toxic metals with the raw materials [35]. The metal pollution index of groundwater (Table 2) shows that the water in the area have different levels of pollution severity for the heavy metals, with the most severe level (highly polluted) being caused by lead.

		•	, .	•
Parameter	Ci	MACi	MPI	Rating
Lead (Pb)	0.090	0.010	9.000	Highly polluted
Iron (Fe)	0.090	0.300	0.300	Lightly polluted
Manganese (Mn)	0.020	0.200	0.120	Lightly polluted
Zinc (Zn)	0.010	3.000	0.000	Very lightly polluted
Nickel (Ni)	0.010	0.020	0.500	Lightly polluted
Chromium (Cr)	0.130	0.050	2.600	Moderately polluted
Copper (Cu)	0.02	1.000	0.020	Lightly polluted

Table 2 Metal pollution index of groundwater samples

Table 3 shows the correlation between the heavy metals. There is a strong positive correlation (0.809) between Pb and Mn, and the relationship between them is significant. There is also a slight moderate positive correlation (0.661) between Pb and Cr. Furthermore, a strong positive correlation (0.873) exists between Mn and Cr.

Table 3 Correlation between heavy metals in the water

				2			
Metals	Pb	Fe	Mn	Zn	Ni	Cr	Cu
Pb	1						
Fe	0.064	1					
Mn	0.809*	0.018	1				
Zn	0.058	0.210	0.267	1			
Ni	0.058	0.052	0.178	0.200	1		
Cr	0.661^{*}	-0.054	0.873**	0.408	0.000	1	
Cu	-0.407	0.188	-0.429	-0.391	-0.260	-0.558	1

*Indicates significant correlation

Since *p* values of the heavy metals in groundwater samples are lower than the significance level (0.05), the null hypothesis (H₀) was therefore rejected (Table 4). This indicates that the heavy metals in the water samples are from different sources.



	Test Value = 0											
Metals	t	df	Sig. (2-tailed)	Mean	95% Confidence Interval of the Difference							
				Difference	Lower	Upper						
Pb	2.776	9	0.022	0.03200	0.0059	0.0581						
Fe	3.932	9	0.003	0.10000	0.0425	0.1575						
Mn	4.811	9	0.001	0.03600	0.0191	0.0529						
Zn	9.000	9	0.001	0.01500	0.0112	0.0188						
Ni	9.000	9	0.001	0.01500	0.0112	0.0188						
Cr	8.573	9	0.001	0.01400	0.0103	0.0177						
Cu	5.468	9	0.001	0.02800	0.0164	0.0396						

Table 4 Results of t test for heavy metals in groundwater samples

4.2 Heavy Metals in Soil and Plant

Table 5 shows the comparison of the average heavy metal levels in soil and plant samples with the suggested elemental background values and crustal abundances [15, 36, 37]. The pollution level from heavy metals is determined by the index of geo-accumulation. Samples with heavy metal concentrations higher than the recommended levels are considered to be contaminated or polluted.

Table 5 Mean concentration of heavy metals in soil and plant with average crustal abundance / background and
standard values [36,15, 37]

Heavy metal	Mean	Mean concent	Decorded			Recorded value by [37]	
	tion in soil (ppm)	ration in plants (ppm)	value by [36]	Recorded value by [15]	Pollution status	Plant	Soil
Lead (Pb)	0.080	0.070	17.000	20.000	Very low	0.2	-
Manganese (Mn)	0.270	0.070	527.000	600.000	Very low	-	
Zinc (Zn)	0.120	0.050	52.000	71.000	Very low	0.5	-
Nickel (Ni)	0.020	0.040	18.600	20.000	Very low	-	
Copper (Cu)	0.030	0.020	14.300	25.000	Very low	0.2	-

Table 6 Calculated index of geo-accumulation (Igeo) for soil and plant samples

Heavy Metal	Igeo Soil	Igeo Plant	Igeo Rating
Lead (Pb)	-8.110	-8.520	Unpolluted
Manganese (Mn)	-10.410	-11.620	Unpolluted
Zinc (Zn)	-8.520	-12.020	Unpolluted
Nickel (Ni)	-9.570	-9.210	Unpolluted
Copper (Cu)	-9.210	-9.320	Unpolluted

Table 5 shows that the concentrations of heavy metals in soil and plants in the research region are within the generally accepted limits of the background values, average crustal abundance, and suggested norms [38]. The use of phytoremediation technique could be the reason for low heavy metal concentrations in the analysed soil and plant samples. From the Igeo data (Table 6), the soil and plants at the research region are not contaminated with lead, manganese, zinc, nickel, or copper.

Met	als	Pb	Mn	Zn	Ni	Cu
Pł)	1				
M	n	0.020	1			
Zı	1	0.070	-0.257	1		
Ν	i	-0.109	-0.045	-0.732*	1	
Сι	ı	-0.185	-0.730*	0.644*	-0.393	1
*India		ignificanc				

 Table 7 Correlations between heavy metals in soil samples

*Indicates significance

The connections between the heavy metals in soil samples (Table 7) established that Zn and Ni have a significant negative association (-0.732). Similarly, Mn and Cu have a high negative connection (-0.730), but Zn and Cu have a moderately positive correlation (0.644).

	Table 8 Results of t test for heavy metals in soil samples												
			Test Va	alue = 0									
Metals	als t		Sig. (2-tailed)	Mean	95% Confide of the Diffe	ence Interval erence							
			0 (Difference	Lower	Upper							
Pb	11.759	9	0.001	0.02600	0.0210	0.0310							
Mn	11.738	9	0.001	0.23200	0.1873	0.2767							
Zn	9.000	9	0.001	0.03900	0.0292	0.0488							
Ni	7.584	9	0.001	0.02100	0.0147	0.0273							
Cu	6.736	9	0.001	0.02200	0.0146	0.0294							

From Table 8, the null hypothesis (H_0) is rejected since the *p* values of the heavy metals in soil samples are below the significant level (0.05). This implies that the heavy metals in the soil samples are distinct from one another and come from various sources.

Table 9	Tests	of Norm	ality
---------	-------	---------	-------

Cail Complex		Kolmogorov–Smirnov					
Soli Samples		Statistic	df	Sig.			
Water samples	0.32	0.260	2	0.003			

As shown in Table 9 and Figure 3, the distribution of heavy metals in the water and soil samples are normal with a *p* value of 0.003, less than the significance level of 0.05.







4.3 Human Risk Assessment

Human risk assessments for the water samples are presented in Tables 10 and 11:

											-			
Stat	Zn		Fe		Mn		١	Ni C		Cr F		Pb Cu		u
	CDDIng	CDD _{Derm}	CDD_{Ing}	CDD _{Derm}	CDDIng	CDD _{Derm}	CDD_{Ing}	CDD _{Derm}	CDDIng	CDD _{Derm}	CDDIng	CDD _{Derm}	CDD _{Ing}	CDD _{Derm}
Min	2.74×10 ⁻	2.98×10⁻	8.22×10-	8.95×10⁻	2.74×10-	2.98×10⁻	2.74×10 ⁻	2.98×10⁻	2.74×10-	2.98×10⁻	2.74×10-	2.98×10⁻	2.74×10-	2.98×10⁻
	4	9	4	᠀	4	᠀	4	᠀	4	᠀	4	᠀	4	᠀
Max	5.48×10-	5.97×10⁻	5.75×10⁻	6.26×10⁻	1.92×10⁻	2.09×10⁻	5.48×10 ⁻	5.97×10⁻	5.48×10 ⁻	5.97×10⁻	2.74×10 ⁻	2.98×10⁻	1.64×10⁻	1.79×10⁻
	4	᠀	₃	⁸	₃	⁸	4	᠀	4	᠀	3	⁸	₃	ଃ
Mea	2.74×10−	2.98×10−	2.47×10-	2.68×10-	5.48×10-	5.97×10-	2.74×10-	2.98×10-	2.74×10-	2.98×10-	2.47×10-	2.68×10-	5.48×10-	5.97×10-
n	₄	9	3	⁸	4	9	4	9	4	9	3	⁸	4	9

 Table 10 Estimated chronic dose of the heavy metals in the water samples for oral and dermal pathways

Table 11 Estimated hazard quotients, hazard index, and incremental lifetime cancer risks of the heavy metals in the water samples

	Zn		Fe	Fe Mi		n Ni		Cr		F	Pb		Cu			
Stat	HQ _{Ing}	HQ _{Derm}	HQ _{Ing}	HQ _{Derm}	HQ _{Ing}	HQ _{Derm}	HQ _{Ing}	HQ _{Derm}	HQ _{Ing}	HQ _{Derm}	HQ _{Ing}	HQ _{Derm}	HQ _{Ing}	HQ _{Derm}	HI	ILCR
Min	9.13×10-4	4.97×10-8	2.74×10 ⁻¹	-	5.96×10-3	1.62×10-6	1.37×10-2	2.43×10-5	9.13×10-2	4.97×10-5	7.83×10-2	5.68×10-6	6.85×10-3	2.49×10-7	0.4711	3.70×10-4
Max	1.83E-3	9.94×10 ⁻⁸	1.92	-	4.17×10 ⁻²	1.13×10 ⁻⁵	2.74×10 ⁻²	4.85×10 ⁻⁵	1.83×10 ⁻¹	9.94×10 ⁻⁵	7.83×10 ⁻¹	5.68×10 ⁻⁵	4.11×10 ⁻²	1.49×10 ⁻⁶	2.9955	7.58×10 ⁻⁴
Mean	9.13×10-4	4.97×10 ⁻⁸	8.22×10-1	-	1.19×10-2	3.24×10-6	1.37×10-2	2.43×10-5	9.13×10-2	4.97×10-5	7.05×10-1	5.11×10 ⁻⁵	1.37×10-2	4.97×10-7	1.6581	3.88×10-4

Tables 10 and 11 list the estimated chronic daily dose (CDD) of the heavy metals via oral and dermal pathways, as well as their carcinogenic (ILCR) and non-carcinogenic (HI) risks. The mean CDD values for oral route ranged between 2.74×10^{-4} (zinc, nickel, and chromium) and 2.47×10^{-3} (lead and iron) mg/L/year, with lead and iron having the highest value. These two elements also have the highest value for the estimated mean of dermal pathway CDD, which varied from 2.98×10^{-9} to 2.68×10^{-8} . This demonstrates unequivocally that the oral channel is the main way that residents are exposed to harmful substances. The risk quotient is the highest for iron, followed by lead, chromium, nickel, copper, manganese, and zinc, according to the hazard quotient (HQ) values computed for oral and dermal pathways. The oral pathway HQ ranged from 9.13×10^{-4} for zinc to 8.22×10^{-1} for iron, whereas the dermal pathway HQ ranged from 4.97×10^{-8} for zinc to 5.11×10^{-1} for lead. The overall hazard index (HI), with an average value of 1.65, varied from 0.4711 to 2.9955. The median HI value exceeds the suggested safe limit of 1 established by USEPA [19]. This indicates that for people who live nearby or inside the research area, the risk of non-carcinogenic consequences is considerable.

For the carcinogenic heavy metals, the incremental lifetime cancer risk (ILCR) ranged from 3.70×10^{-4} to 7.58×10^{-4} with an average value of 3.88×10^{-4} . The permissible range for cancer risks is between 1.00×10^{-6} and 1.00×10^{-4} , with cancer risks above 1.00×10^{-4} being regarded as high and values below 1.00×10^{-6} being regarded as not posing any risk of cancer to humans. Thus, the mean cancer risk is within the acceptable limits. Lead is the main contributor to the cancer risk, followed by chromium and nickel. As previously mentioned, this significant lead concentration may be the result of emissions from power plants after using coal as a substitute energy source during cement manufacturing [31–33]. Therefore, the indiscriminate discharge of untreated industrial effluents, or the association of these toxic metals with the raw materials, which typically consist of iron oxide, lead, copper, manganese, and chromium [54] and the use of coal as a substitute for other sources of energy during cement production [31], are the causes of the high HI risk values for the water samples. The general population is urged to purify their water before using it for drinking or other domestic purposes because the risk of non-carcinogenic consequences is considerable for people living in the research region. These harmful metals can be removed from contaminated water using techniques such as electrochemical treatment, chemical precipitation, membrane filtration, ion exchange, reverse osmosis, adsorption, or solvent extraction.

5. Conclusion

Untreated industrial effluent discharge has a detrimental influence on the environment and poses a risk to human health. The quality of groundwater, soil, and plant life near a cement production site in Obajana was assessed in this study, which serves as a baseline investigation into the impact of industrial wastes on the environment in the studied region. Water, soil, and plant samples were examined for the presence of heavy metals. With the exception of lead, whose concentration was above the recommended level, the analysis demonstrates that iron, manganese, zinc, nickel, chromium, and copper concentrations in the water samples were within the acceptable limits based on NSDWQ and average crustal abundance/background values. High amount of lead may be due to emission from the power plant.

The non-carcinogenic risk assessment yielded values that are higher than the allowed limits, whereas the carcinogenic risk assessment gave values that are within the advised range. This demonstrates that the heavy metals pose a non-carcinogenic health risk to the public. According to the average crustal abundance and background values, the concentrations of heavy metals in soil and plant samples are below allowable limits, indicating that the soil and plants in the research region are not contaminated by the heavy metals studied. The current study suggests ongoing groundwater, soil, and plant monitoring in the area, while industries ought to be ecologically aware to stop more harm. The mechanism of environmental pollution should be explained in depth, with a focus on untreated harmful industrial effluents in particular.

Acknowledgement

We would like to thank all the parties involved in making this project possible.

Conflict of Interest

The authors confirmed that there is no conflict of interest.

Author Contribution

All of the authors who participated personally and actively in the design, data collection, analysis, interpretation, writing, and submission of this publication made significant contributions to it.



References

- [1] Afolabi, A., Francis, F. A., & Adejompo, F. (2012). Assessment of health and environmental challenges of cement factory on Ewekoro community residents, Ogun State, Nigeria. *American Journal of Human Ecology*, 1(2), 51–57. https://doi.org/10.11634/21679622150479
- [2] Sirajudeen, J., Arulmanikandan, S., & Manivel, V. (2015). Heavy metal pollution index of groundwater of Fathima Nagar area near Uyyakondan channel Tiruchirappalli district, Tamil Nadu, India. *World Journal of Pharmacy and Pharmaceutical Sciences* (WJPPS), 4(1), 967–975.
- [3] Bhutiani, R., Kulkarni, D. B., Khanna, D. R., & Gautam, A. (2017). Geochemical distribution and environmental risk assessment of heavy metals in groundwater of an industrial area and its surroundings, Haridwar, India. *Energy, Ecology and Environment*, 2, 155–167. https://doi.org/10.1007/s40974-016-0019-6
- [4] Abdulkadir, S., Sanda, A. R., Musa, M. U., Adamu, U. K., & Nasiru, A. N. (2020). Discharged industrial effluents quality appraisal and its uses for agricultural production in Sudan Savannah Ecological Zone, Nigeria. *Journal of Environmental Science, Technology and Food Technology*, 14(3), 45–51. https://doi.org/10.9790/2402-1403014551
- [5] Mohankumar, K., Hariharan, V., & Rao, N. P. (2016). Heavy metal contamination in groundwater around industrial estate vs residential areas in Coimbatore, India. *Journal of Clinical and Diagnostic Research*, 10(4), BC05–BC07. https://doi.org/10.7860/JCDR/2016/15943.7527
- [6] Balogun, E. S. (2016). An assessment of the impact of Obajana cement factory on the socio-economic development of Obajana, Kogi State, Nigeria (Unpublished Master Thesis, Ahmadu Bello University, Zaria, Nigeria).
- [7] Aukour, F. J., & Al-Qinna, M. I. (2008). Marble production and Environmental Constraints: Case study from Zarqa Governorate, Jordan. *Jordan Journal of Earth and Environmental Sciences*, 1(1), 11–21.
- [8] Ho, Y. C., Show, K. Y., Guo, X. X., Norli, I., Abbas, F. A., & Morad, N. (2012). Industrial discharge and their effect to the environment. *Industrial Waste*, 1–33.
- [9] Meme, F. K., & Nwadukwe, F.O. (2016). Impact assessment of cement factory waste water on the heavy metal contents of a typical low-latitude stream in Northcentral Nigeria. *Chemistry and Materials Research*, 8(5), 42–48.
- [10] Abdullateef, J. O., Elueze, A. A., & Ahmed, J. B. (2014). Geochemistry and economic potential of marble from Obajana, north central, Nigeria. *Advances in Applied Science Research*, *5*(3), 146–151.
- [11] Vetiva, A. (2010). The emergence of a titan: Dangote cement PLC–Initiation of coverage. Capital Management Limited.
- [12] Obaje, N. G., & Abaa, S. I. (1996). Potential for coal derived gaseous hydrocarbon in middle Benue trough of Nigeria. *Journal of Petroleum Geology*, *19*(1), 77–94. https://doi.org/10.1111/j.1747-5457.1996.tb00514.x
- [13] Nigerian Standards for Drinking Water Quality. (2017). p.15-17
- [14] Udoh, B. O., & Amadi, A. N. (2020). Evaluation of heavy metal pollution level in soils and plants around Ibeno area, Akwa-Ibom State, Niger Delta, Nigeria. *Pacific Journal of Science and Technology*, 21(1), 290– 303.
- [15] Taylor, S. R., & McLennan, S. M. (1995). The geochemical evolution of continental crust. *Reviews of Geophysics*, 33(2), 241–265. https://doi.org/10.1029/95RG00262
- [16] Müller, G. (1981) The heavy metal pollution of the sediments of neckars and its tributary: A stocktaking. *Chemiker Zeitung*, 105, 157–164.
- [17] United State Environmental Protection Agency. (2004). Risk assessment guidance for superfund volume I: Human health evaluation manual (Part E, supplemental guidance for dermal risk assessment (final). https://www.epa.gov/risk/risk-assessment-guidance-superfund-rags-part-e
- [18] Singh, A., Maichle, R., Singh, A. K., Lee, S., & Armbya, N. (2007). ProUCL version 4.00.02 user guide. United State Environmental Protection Agency. https://www.epa.gov/sites/default/files/2015-03/documents/proucl_v4.00.02_user.pdf
- [19] United State Environmental Protection Agency. (2009). Risk assessment guidance for superfund volume I: Human health evaluation manual (Part F, supplemental guidance for inhalation risk assessment). https://www.epa.gov/risk/risk-assessment-guidance-superfund-rags-part-f
- [20] United State Environmental Protection Agency. (2011). *National primary drinking water regulations*. http://water.epa.gov/drink/contaminants/index.cfm#List
- [21] United Nuclear Corporation. (2011). Updated baseline human health risk assessment.
- [22] Office of Emergency and Remedial Response. (2001). Guidance for characterizing background chemicals in soil at superfund sites (OSWER Directive 9285:7 – 41). United State Environmental Protection Agency, Washington, DC.
- [23] Division of Toxicology and Human Health. (2012). *Public health statement on Cadmium* (p.1 10). Agency for Toxic Substances and Disease Registry, Atlanta, USA.



- [24] Orosun, M. M., Adewuyi, A. D., Salawu, N. B., Isinkaye, M. O., Orosun, A. R., & Oniku, A. S. (2020). Monte Carlo approach to risks assessment of heavy metals at automobile spare part and recycling market in Ilorin, Nigeria (Scientific Report 10: 22084). https://doi.org/10.1038/s41598-020-79141-0
- [25] Orosun, M. M. (2021). Assessment of arsenic and its associated health risks due to mining activities in parts of North-central Nigeria: Probabilistic approach using Monte Carlo. *Journal of Hazardous Materials*, 412, 125262. https://doi.org/10.1016/j.jhazmat.2021.125262
- [26] World Health Organization. (2017). Guidelines for drinking water quality.
- [27] Rinklebe, J., Antoniadis, V., Shaheen, S. M., Rosche, O., Altermann, M. (2019). Health risk Assessment of potentially toxic elements in soils along the Central Elbe River, Germany. *Environment International*, 126, 76–88. https://doi.org/10.1016/j.envint.2019.02.011
- [28] Isinkaye, O. M. (2018). Distribution and multivariate pollution risks assessment of heavy metals and natural radionuclides around abandoned iron-ore mines in North Central Nigeria. *Earth Systems and Environment*, 2(2), 331–343. https://doi.org/10.1007/s41748-018-0035-0
- [29] Tesi, G. O., Iniaghe, P. O., Lari, B., Obi-Iyeke, G., & Ossai, J. C. (2021). Polycyclic aromatic hydrocarbons (PAHs) in leafy vegetables consumed in southern Nigeria: concentration, risk assessment and source apportionment. *Environmental Monitoring and Assessment, 193*(7), 443. https://doi.org/10.1007/s10661-021-09217-5
- [30] Zeng, F., Wei, W., Li, M., Huang, R., Yang, F., & Duan, Y. (2015). Heavy metal contamination in rice-producing soils of Hunan province, China and potential health risks. International Journal of Environmental Research and Public Health, *12*(12), 15584–15593. https://doi.org/10.3390/ijerph121215005
- [31] Chowdhury, I. R., Chowdhury, S., Mazumder, M. A. J., & Al-Ahmed, A. (2022). Removal of lead ions (Pb2+) from water and wastewater: A review on the low-cost adsorbents. *Applied Water Science*, 12(8), 185. https://doi.org/10.1007/s13201-022-01703-6
- [32] Cabral-Pinto, M. M., Inácio, M., Neves, O., Almeida, A. A., Pinto, E., Oliveiros, B., & Ferreira da Silva, E. A. (2020). Human health risk assessment due to agricultural activities and crop consumption in the surroundings of an industrial area. *Exposure and Health*, 12, 629–640. https://doi.org/10.1007/s12403-019-00323-x
- [33] Kumar, A., Cabral-Pinto, M., Kumar, A., Kumar, M., & Dinis, P. A. (2020). Estimation of risk to the ecoenvironment and human health of using heavy metals in the Uttarakhand Himalaya, India. *Applied Sciences*, 10(20), 7078. https://doi.org/10.3390/app10207078
- [34] Jordão, C. P., Pereira, M. G., & Pereira, J. L. (2002). Metal contamination of river waters and sediments from effluents of kaolin processing in Brazil. *Water, Air, and Soil Pollution, 140,* 119–138. https://doi.org/10.1023/A:1020179223867
- [35] Adejoh, I. P. (2016). Assessment of heavy metal contamination of soil and cassava plants within the vicinity of a cement factory in north central, Nigeria. *Advances in Applied Science Research*, 7(3), 20–27.
- [36] Wedepohl, K. H. (1995). The composition of the continental crust. *Geochimica et Cosmochimica Acta*, 59(7), 1217–1232. https://doi.org/10.1016/0016-7037(95)00038-2
- [37] National Agency for Food and Drug Administration and Control. (2018). *The national guidelines and standards for water quality in Nigeria.*

