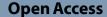
RESEARCH



Spatial distribution of heavy metals in groundwater around automobile workshops in a popular Niger-Delta University town, Nigeria

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Abstract

The research was carried out to assess the concentration and distribution of heavy metals in groundwater from selected automobile workshops in Ozoro metropolis, a busy university town, in the Niger Delta region of Nigeria. The major activities carried out in the sampled automobile workshops include vehicle maintenance, painting, panel beating and fabrication. Nine (9) groundwater samples from the automobile workshops and one control sample 2 km away from the influence area were analyzed. Heavy metal concentration, contamination factor, and pollution loading indices were investigated using geostatistical modeling and statistical analysis tools. Heavy metal concentrations in the various samples were determined in accordance with the Association of Official Agricultural Chemists (AOAC) International guidelines. Findings obtained from the study revealed that the groundwater was affected by leachates from the automobile workshops, as the heavy metal levels in the groundwater from the sampling sites were considerably higher than the reference point. The concentration ranges (mg/L) of the heavy metals were Cd (0.0217-0.0412), Cr (0.0643-0.0901), Cu (0.0599-0.0803), Fe (0.3118-0.4171), and Pb (0.1423-0.1781). The spatial distribution maps showed that the metals spread unevenly across the study area. The pollution indices revealed that groundwater from the sampling sites is moderately polluted with heavy metals and the trend of the pollution load index (PLI) is Cd > Ni > Cu > Mn > Pb > Zn > Fe. Comparing the results with those of international regulatory bodies, the groundwater from the study area was found to still be within the approved range for potable water. However, there is evidence of slight contamination due to the activities of the automobile workshops. This may call for minor treatment before usage, regular monitoring and ensuring that the artisans comply with relevant regulations in their operations.



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Highlights

• Effects of automobile workshop activities on Ozoro community groundwater were evaluated.

• Findings revealed the groundwater was affected by leachates from the workshop activities.

• Cd, Cr, Cu, Fe and Pb level varied from 0.0643–0.0901 mg/L, 0.0599–0.0803 mg/L, 0.0217–0.0412 mg/L, 0.3118–0.4171 mg/L and 0.1423–0.1781 mg/L, respectively.

• Spatial distribution maps depicted that the metals spread unevenly across the community.

• Trend of the water Pollution Load Index (PLI) is Cd > Ce > Ni > Cu > Mn > Pb > Zn > Fe.

Keywords: Automobile workshop, Contamination, Groundwater quality, Heavy metals, Leachates, Niger Delta

Introduction

Environmental pollution is the discharge of toxic substances into the environment, which has significant consequences for the natural ecosystem [2-6]. In many countries of the world, pollution resulting from indiscriminate discharge of heavy metals [7, 12, 13, 47] as well as petroleum and its derivatives [32, 43, 63] into the environment is a major source of environmental pollution. More than ever before, pollution-related diseases have risen, as more than one in every four deaths is linked to pollution [48]. According to Muze et al. [57], environmental pollution does not only affect the health performance of plants and animals, it also alters the physiochemical properties of groundwater and affects the soil's geotechnical properties [20]. Research carried out by Akinwumi et al. [8] revealed that petroleum contamination of the soil causes a substantial increase in the soil's plasticity and a reduction in its shear strength. Heavy metal pollution of the environment has increased in recent times due to increased anthropogenic activities in agriculture, mining, and industrial processes [14, 40]. A major source of heavy metal pollution in the environment that significantly affects water quality and soil engineering properties is the effluent from artisans' automobile workshops [61]. In Nigeria, there has been a dramatic increase in the population of automobile workshops due to the high influx of used vehicles and old vehicle engines into the country from developed countries [61]. Furthermore, the lack of environmental regulatory agencies, monitoring the activities of these artisans has contributed to the increase in their population in society. The major activities carried out by these artisans in automobile workshops include vehicle maintenance, painting, panel beating and fabrication. Automobile (repair) workshops release waste products such as engine oil, transmission oil, brake fluid, damaged tires, battery electrolyte, wire carbide, spent batteries, and cells into their surrounding areas. This indiscriminate disposal leads to the discharge of toxic emissions during abrasion and contributes to metal contamination of areas within the auto-repair workshops [17, 31, 33–35]. Several studies have been carried out to evaluate the effect of automobile workshops on the environment [1, 15, 37, 53, 61]. Prominent among the heavy metals released from auto-repair (automobile) workshops are copper, chromium, cadmium, lead, mercury, silver, cobalt, iron, zinc, and arsenic [5, 26]. These heavy metals are known to pollute ground water, posing severe health risk to people [18, 19].

Groundwater receives its heavy metal contamination either through natural deposition or anthropogenic actions [22, 77]. Groundwater plays significant roles in human lives as they serve both domestic and agricultural purposes. Hence, polluting groundwater with heavy metals makes it difficult for a good number of people to have access to safe drinking water [54, 71]. The discharge of these metals into the environment pollutes groundwater and has lasting effects on the ecosystem and public health [20, 27–29, 47, 78]. Even in dilute concentrations, heavy metals are toxic because they are not degradable and accumulate in living cells [49, 65, 84]. Some ailments associated with heavy metal toxicity in human bodies are liver problems, kidney failure, respiratory problems, and vision impairment [11, 73].

Due to the collapse of the public water supply system, the residents of Ozoro metropolis rely on private boreholes and hand-dug wells for their drinking water [77]. Since the majority of the residents of the study area consume the water in its untreated state, it is important to assess the impact of any activity that can impact the quality of groundwater in such an environment. However, based on the information available to the authors during this research, there are no available data on heavy metal contamination indices in groundwater within and around automobile workshops in the study area. This study is therefore aimed at assessing the extent of heavy metal contamination in groundwater due to the activities in automobile workshops within Ozoro metropolis, studying the heavy metals' distribution, analyzing the factors of distribution, and evaluating the correlation between heavy metals in the samples and the control. This will help in ascertaining the health risk level of groundwater in the study area so as to recommend appropriate remediation techniques in order to enhance the quality of drinking water.

Methods

Study area

The study was carried out in the university environment of Ozoro Delta State, in the Niger-Delta Area of Nigeria. Ozoro is the administrative headquarters of the Isoko North Local Government Area. It has a geographical coordinate of latitude 5'30 and 6'54'' North and longitude 6'54'' and 7'54'' East, as shown in Fig. 1. Ozoro is a rapidly developing town with a population of about 158,364 people [70].

Located within the Ozoro community are the Delta State University of Science and Technology, several small and medium-scale businesses, an oil-producing company, etc. The area has several clusters of vehicle (automobile) maintenance workshops, as shown in Figs. 2 and 3, with operation ages ranging between 2 and 15 years. Their maintenance activities include welding and panel beating, engine repair, spraying and painting, and electrical part repairs. Most of the wastes (scrap metals, petroleum products, carbide, paints, and waste acids) generated by these artisans are discarded untreated into the environment.

Sample collection

Nine (9) automobile workshop clusters within the Ozoro community were randomly sampled for the study. The geographical coordinates of the clusters are presented in

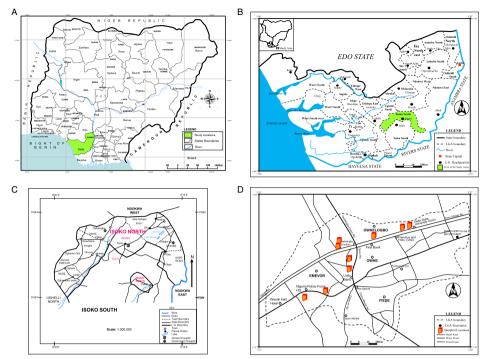


Fig. 1 Map of Nigeria showing Ozoro Community



Fig. 2 A vehicle mechanic workshop at Ozoro

Table 1. Within the vicinity of these clusters, there was no presence any other major industrial activity; thus, the only other anthropogenic activity that could interfere with groundwater quality is the effluent from the private toilet facilities. Another point (reference or control point) was selected 2 km from the study area, with no history of



Fig. 3 A Panel beating workshop

Cluster point	Geographical coordinates				
	Latitude	Longitude			
Point A	5°33′18.36″	6°14′44.15″			
Point B	5°33′17.28″	6°33′17.28″			
Point C	5°33′14.76″	6°14′19.68″			
Point D	5° 2′54.59″	6°13′40.08″			
Point E	5°32′27.96″	6°13′36.48″			
Point F	5°31′52.32″	6°12′40.31″			
Point G	5° 33′ 1.44″	6°13′ 37.56″			
Point H	5° 33′2.52″	6°13′36.84″			
Point I	5°32′45.96″	6°13′59.16			

 Table 1
 Cluster points coordinates

automobile workshops or oil spills. At each cluster, water was sampled from three boreholes using pre-sterilized plastic bottles, placed in an ice box, and taken immediately to the laboratory for heavy metal analysis.

Laboratory analysis

Digestion of the water sample

The water was initially filtered with filter paper, and 100 mL of the filtered water was acidified with 5 drops of concentrated trioxonitrate (V) acid. The acidified water was evaporated in a water bath to a volume of 15 mL, removed from the water bath, allowed to cool to room temperature, and diluted with distilled water to 100 mL [16].

Heavy metals measurement

The presence and concentrations of Cd, Ni, Pb, Co, and Zn in the digested water sample were determined using the atomic absorption spectrometry (AAS) in accordance with the AOAC guidelines.

Pollution indices evaluation

Contamination factor (CF)

The water CF was calculated through the formula shown in Eq. 1 [55].

$$CF = \frac{C_x}{C_n} \tag{1}$$

where:

 $C_x = C$ oncentration of the pollutant in the sediment or water samples, and $C_n = C$ oncentration of the heavy metal at the control. CF interpretation: [55]. CF < 1 = low contamination, 1 < CF < 3 = moderate contamination, 3 < CF < 6 = considerable contamination, CF > 6 = high contamination

Pollution load index (PLI)

The water PLI was calculated through the expression given in Eq. 2.

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times CF_3 \times CF_4 \times \dots \times CF_n}$$
(2)

where:

CF = each heavy metal contamination factor, and n = number of heavy metals [39].

PLI values are interpreted as:

PLI < 1 = unpolluted PLI = 1 baseline level of pollution 1 > PLI \leq 2 moderately polluted 2 > PLI \leq 4 highly polluted PLI > 4 very highly polluted

Geostatistical modelling

The spatial distribution of heavy metals concentration in the sampled water across the study region was done using geostatistical tools. Geostatistics uses variograms to ascertain the spatial variableness of a regionalized variable and gives the input data for Kringing modeling [46].

Statistical analysis

The data obtained from this study were analyzed using tables and bar charts, while the Pearson correlation was used to establish the correlation relationship between the concentrations of the heavy metals and their possible sources of contamination.

Results and discussion

Assessment of water quality

The results of the groundwater heavy metals distribution is presented in Table 2. It was noted that the heavy metals level in the control point was considerably lower than those from the various spatial points. Spatially, points G and D had the highest and lowest Cd concentrations respectively. The maximum and minimum Cr concentrations were recorded at locations F and E, respectively, while points F and A had the highest and lowest Cu levels, respectively. Also, the highest and least Fe levels were recorded at spatial points F and H, respectively, while locations E and A had the highest and lowest Pb levels, respectively. Locations C and I recorded the maximum and minimum Mn levels, respectively while locations F and H had the highest and lowest Ni concentrations, respectively. The spatial points C and I recorded the highest and lowest Zn concentrations, respectively. The lead concentration record in this study was lower than the results reported by Bala et al. [23] and Oloruntoba and Ogunbunmi [61] for effluents impacted groundwater samples. Furthermore, the high metals level in the groundwater sampled from the vicinity of mechanic workshop corroborates findings of Talabi and Kayode [72] and Nwachukwu et al. [59], which stated that leachates from chemicals and vehicle mechanic workshops have the ability to contaminate groundwater.

The degree of heavy metals concentration in the region's groundwater followed this trend: Fe > Ni > Zn > Pb > Cd > Cr > Cu > Mn. This indicates that Fe had the highest concentration in groundwater, while Mn had the least concentration in the region's groundwater. The high Zn, Pb and Cd level in the groundwater could be linked to leachates from petroleum products into the groundwater; while the high Fe, Mn and Ni content can be attributed to the leachates from the metallic components of the vehicles waste (condemned) parts [38, 41, 42]. Petroleum hydrocarbons can increase Cd and Pb concentration of water bodies [78], while scrap metals effluent dramatically increased the groundwater heavy metals concentration [30]. Similarly Ilemobayo and Kolade [44] and Pam et al. [64] in their investigations into the activities of artisans' workshops, reported

Table 2 Heavy metal concentration (mg/
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	Point A	Point B	Point C	Point D	Point E	Point F	Point G	Point H	Point I	Control
Cd	0.07	0.08	0.07	0.06	0.07	0.08	0.09	0.08	0.07	0.00
Cr	0.07	0.06	0.06	0.06	0.06	0.09	0.06	0.07	0.08	0.00
Cu	0.04	0.03	0.02	0.03	0.02	0.02	0.03	0.02	0.02	0.01
Fe	0.39	0.39	0.39	0.43	0.41	0.42	0.31	0.31	0.35	0.18
Pb	0.14	0.15	0.17	0.18	0.18	0.17	0.17	0.15	0.17	0.04
Mn	0.02	0.02	0.02	0.02	0.20	0.02	0.20	0.02	0.20	0.00
Ni	0.21	0.23	0.22	0.21	0.21	0.22	0.23	0.21	0.21	0.03
Zn	0.22	0.23	0.23	0.20	0.23	0.22	0.21	0.19	0.19	0.10

Table 3 WHO permissible limit of heavy metals

Heavy metals	Cd	Cr	Cu	Fe	Pb	Mn	Ni	Zn
Allowable limits (mg/l)	0.05	0.003	2	0.3	0.01	0.1	0.1	3

Table 4 Correlation relationship between the heavy metal

	Cd	Cr	Cu	Fe	Pb	Mn	Ni	Zn
Cd	1							
Cr	0.193	1						
Cu	-0.002	-0.376	1					
Fe	-0.634	-0.034	0.003	1				
Pb	-0.126	-0.085	-0.536	0.279	1			
Mn	0.228	0.059	-0.419	-0.312	-0.372	1		
Ni	0.7	-0.029	0.358	-0.172	-0.069	-0.083	1	
Zn	0.11	-0.338	0.332	0.392	-0.096	0.114	0.488	1

that effluents which are discharged from mechanic villages contain numerous toxic heavy metals that will alter the heavy metals concentration of the groundwater.

Furthermore, the finding revealed that despite the higher values of heavy metals concentration in the spatial locations above the control point, the heavy metal level in the water never exceeded the WHO approved limits for drinking water. Similar, results were obtained by Uguru et al. [77] for groundwater samples from Ozoro community. Uguru et al. [77] stated that though groundwater quality was adversely affected by anthropogenic actions, most of the heavy metals concentration was within the [81] approved allowable limit for water portability as presented in Table 3.

Heavy metal correlation analysis

The results of the heavy metals Pearson correlation analysis is presented in Table 4. The result depicted that there is a strong relationship between Cd and Ni (r=7), indicating that the two pollutants may likely come from the same source, which is petroleum hydrocarbons. Uguru et al. [77, 78] reported that petroleum products contamination can be linked to Cd and Ni contamination of the environment. Also the correlation results revealed that there was fair strong relationship between Cd and Fe, and Cu and Pb. This portrayed that there is likelihood that these metals originated from the mechanic workshops in the samples location, probably the scarp vehicle parts effluent. Furthermore, the results indicated that the relationship among Zn and the other heavy metals evaluated in this study was weakly positive and negative. This depicted that most of the metals and Zn did not originate from the same source, and increment in the Zn level in the water will not cause significant increment in the other metals concentration.

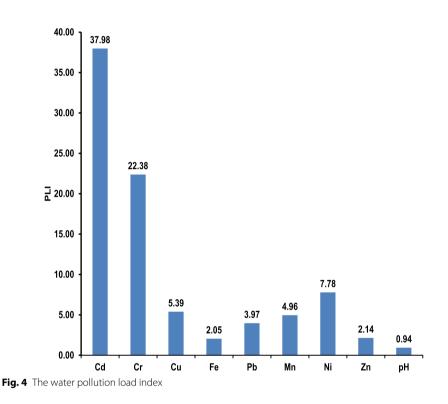
Groundwater pollution rate

Contamination factor

Table 5 shows contamination degree of the heavy metals in the study area groundwater. The results revealed that Cd, Ni and Cr were at high degree of contamination level within

Metal	Point A	Point B	Point C	Point D	Point E	Point F	Point G	Point H	Point I
Cd	35.65	40.10	35.90	32.15	37.24	40.61	45.05	40.95	35.75
Cr	21.77	20.47	19.97	20.07	19.93	29.73	20.97	23.72	26.77
Cu	8.24	6.76	4.54	5.56	4.68	4.34	6.34	4.52	4.76
Fe	2.12	2.11	2.07	2.36	2.25	2.28	1.71	1.70	1.93
Pb	3.47	3.71	4.01	4.30	4.34	4.04	4.18	3.67	4.08
Mn	4.85	4.98	5.33	4.73	4.85	5.03	4.83	5.28	4.84
Ni	7.69	8.25	7.71	7.51	7.63	7.97	8.28	7.48	7.58
Zn	2.27	2.28	2.30	2.01	2.28	2.22	2.17	1.91	1.91

 Table 5
 Heavy metals contamination factor showing contamination degree



the study region (Cf > 6), while Mn and Pb were at considerable degree of contamination (3 < Cf > 6). Furthermore, Zn and Fe were at moderate degree of contamination with the area under this research investigation (1 < Cf > 3). Copper was at high degree of pollution at spatial Points A, B and G, while spatial Points C, D, E F, H and I recorded considerable degree of Cu contamination. The contamination factor analysis showed that none of the spatial point ground water had low heavy metals contamination degree (Cf < 1).

Pollution load index

The results of the heavy metals pollution load index (PLI) are shown in Fig. 4. The findings indicated that the groundwater PLI values range from 0.937 to 37.978 across the sampling locations. Individually, the groundwater is moderately polluted (PLI $^{>}$ 4) with Cd, Cr, Cu, Mn and Ni; while in terms of the Fe, Zn and Pb, the groundwater is slightly polluted with the three heavy metals (2 ^{$^{\circ}}PLI \leq 4$). This portrayed that the groundwater is polluted with toxic metals such as: Cd, Cr, Ni, Zn and Pb. The moderately high PLI values obtained in this study is an affirmation that effluents from anthropogenic activities, probably from the auto mobile maintenance workshop, are the major pollutants in the area. Similar reports were made by Oloruntoba and Ogunbunmi [61], where leachates from vehicle maintenance workshops caused major damage to the groundwater quality.</sup>

Though some heavy metals (Fe, Cu and Mn) are beneficial to human beings at small quantity, others such as Ni, Pb, Cd are lethal to human beings even at minute quantity [62, 66–69]. Large dosage of toxic heavy metals can lead to kidney and liver failures, gastrointestinal disease, brain damage and cancer [74–76, 79–83, 85]. Fatoki et al. [36] reported that high Pb assimilation can result to stillbirth and children developing neurological problems. Cadmium pollution is a major concern to environmentalists, due to the carcinogenicity effect of Cd as reported by Lauwerys [50].

Spatial distribution of the heavy metals concentration

The spatial distribution maps of Cd and Cu concentrations in the study region are presented in Fig. 5a and b, respectively. Figure 5a reveals that Cd varied widely across the region, with the maximum Cd value observed in the eastern and south-western parts of the area. Similarly, the Cu concentration map presented in Fig. 5b depicts that the Cu content of the groundwater increased non-linearly from the southern-western part of the community to the north-eastern part of the community.

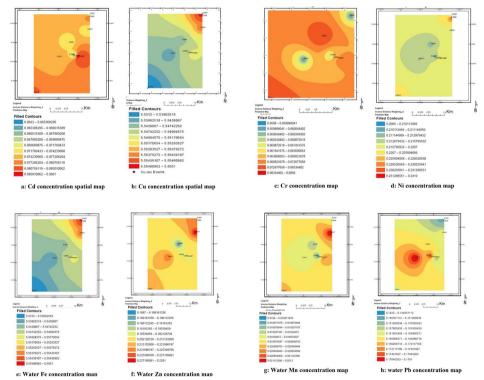


Fig. 5 a Cd concentration spatial map. b Cu concentration spatial map. c Cr concentration map. d Ni concentration map. e Water Fe concentration map. f Water Zn concentration map. g Water Mn concentration map. h Water Pb concentration map

Also, Fig. 5c and d show the spatial distribution of Cr and Ni level across the study region. As shown in Fig. 5c, the Cr content in the water increased non-uniformly from the center part of the community to the boundaries of the community. This indicates that the center of the community had the lowest water Cr level, while the end of the community recorded a higher level of Cr concentration, even though the north-eastern part of the region tends to have a low Cr concentration. Similarly, the spatial map for Ni concentration (Fig. 5d) depicted that the Ni level in the groundwater increased unevenly from the center part of the community to the end part of the community, with the north-eastern part of the community having the peak Ni water concentration.

Furthermore, Fig. 5e, f, g, and h reveal the spatial distribution of Fe, Zn, Mn, and Pb concentrations, respectively, across the area under investigation. The water map in Fig. 5e revealed that the water Fe level increased non-uniformly from the southwestern part of the community to the north-eastern part of the community. The variation in Fe contribution is similar to the Cu concentration within the study region, although the Cu level tends to decline in the community center. Figure 5f illustrates the water map of Zn levels in the community's groundwater. As shown in Fig. 5f, the north-eastern and south-western parts of the study area tend to have higher Zn levels when compared to the other parts. It was also noted that most of the groundwater had a low Zn concentration, with the north-central part having the lowest groundwater Zn concentration.

Figure 5g revealed that the groundwater Mn concentration spread un-evenly from the center of the community to the end part of the community, with the northeastern region groundwater having the maximum Mn level. The spatial distribution map further revealed that most of the groundwater has a moderate Mn concentration. Likewise, the spatial variation map for the groundwater Pb (Fig. 5h) depicts that the Pb concentration declines non-uniformly from the center of the community to the end of the community. The map further revealed that the northeastern part of the water has the lowest Pb concentration. It was noted that the spatial distribution of Pb was similar to the Ni distribution, with the major difference being that Ni had the maximum concentration in the northeastern water as against the lowest Pb content recorded in the northeastern water [45, 46, 51, 52, 56, 60].

The non-uniformity generally observed in the distribution of the heavy metals across the area could be linked to the concentration and volume of the metallic ions at the various locations. According to Akpomrere and Uguru [10], the volume and concentration of leachates affect the concentration of groundwater metals and, subsequently, their distribution in the surface and groundwater. These results are similar to those obtained by Akpomrere and Uguru [10] and Naveen et al. [58]. The authors reported that the metal content in groundwater unevenly declined as the spatial points of sample collection tended to be far away from the suspected polluting source(s).

The lower concentration generally observed in most metals at the end of the community can be attributed to the vegetation in these areas that would have provided preliminary remediation of the toxic leachates and the soil type that hinders the movement of these metallic ions through the soil [21, 24]. Akpomrere and Uguru [9] reported that plants have the ability to degrade toxic metals through phytoremediation, lowering their concentration in the process and thus weakening their potential to contaminate groundwater. Relatively, Barceloux [25] stated that soil with a high proportion of fine grain particles poses a strong adsorption rate for most metals, reducing their toxicity effects in the environment.

Conclusion

This research was conducted to assess the effect of automobile workshops on groundwater quality. Although the concentrations of Cd, Cr, Cu, Fe, Pb, Mn, Zn, and Ni in the sampled groundwater were lower than the WHO-approved levels, it was revealed that the leachates from the workshops compromised the groundwater quality. From the eight metals investigated, Fe had the highest concentration, while Mn had the lowest concentration in the groundwater. Findings from the contamination factor indicated that the region's groundwater was moderately contaminated, while the PLI followed this pattern: Cd > Ni > Cu > Mn > Pb > Zn > Fe. The relatively high contamination level recorded in the groundwater should be considered a potential health hazard because the accumulation of these toxic metals in the body has a lot of negative health implications. Based on these research findings, the Nigerian environmental regulatory agencies should build a major automobile workshop in the region where their activities such as vehicle maintenance, painting, panel beating, fabrication, and others can be carried out and their waste remediated before disposal. This is to avert a possible outbreak of heavy metal toxicity. Furthermore, the groundwater from the region should be subjected to cheap and effective treatments like adsorption and ion-exchange in order to reduce the concentration of heavy metals to permissible levels.

Abbreviations

AAS	Atomic Absorption Spectrophotometry
AOAC	Association of Official Agricultural Chemistry
Cd	Cadmium
CF	Contamination Factor
Cr	Chromium
Cu	Copper
Fe	Iron
Mn	Manganese
Ni	Nickel
Pb	Lead
PLI	Pollution Load Indices
WHO	World Health Organization
WQA	Water Quality Association
Zn	Zinc

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Authors' contributions

TOA and HIO conceived the study idea and established the guiding framework. The laboratory work, data gathering and analysis were coordinated by TOA, HIO. SCI, TOA and EA drafted the original manuscript and organized the data obtained for better clarity and understanding. HIO, HOO and SO edited the English of the manuscript after drafting. All authors read and approved the final manuscript. TOA and SCI handled the submission processes and correspondences. HIO, TOA, HOO and SO critically revised the manuscript after first review.

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Availability of data and materials

It will be made available on request.

Declarations

Competing interests There is no conflict of interest.

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