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Impact of effluent-derived heavy metals on the groundwater quality in Ajao industrial area, Nigeria: an assessment using entropy water quality index (EWQI)

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Abstract

Several numerical models have been utilized in water quality assessments for various purposes. Among all the commonly used models, entropy-weighted water quality index (EWQI) has been recognized as the most unbiased model for assessing drinking water quality. Therefore, this paper presents a case study of the application of EWQI in assessing the effect of effluent-derived heavy metals on the groundwater quality in Ajao industrial estate, Nigeria. Three environmental pollution risk assessment tools were integrated to better evaluate the level of heavy metals contamination in the groundwater. Geoaccumulation index (I_{geo}) placed 66% of the samples in uncontaminated to moderately contaminated category. However, 19% showed moderate to heavy contamination, whereas 14.29% were heavily contaminated. Similarly, enrichment factor (EF) revealed that 52% of the samples have minimal enrichment, 33% are moderately enriched, while 14.29% were extremely enriched with heavy metals. Vector modulus of pollution index (PI_{vector}) showed that the majority of the samples (80.9%) have low pollution, 4.76% recorded moderate pollution, while 14.29% had considerable to very high pollution. The EWQI showed that the majority (85.71%) of the groundwater samples are excellent drinking water, while 14.29% are unsuitable for drinking. However, a dendrogram integrating the results of the I_{geo} , EF, PI_{vector}, and EWQI was produced by hierarchical cluster analysis to harmonize and demarcate the groundwater quality in this industrial area. Although this study confirms the suitability of most samples for drinking, more awareness programs towards the protection of the groundwater should be embraced.

Keywords Environment risk assessment \cdot Entropy water quality index (EWQI) \cdot Groundwater \cdot Hierarchical cluster analysis (HCA) \cdot Lagos

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Introduction

All over the world, underground water has remained the most desirable source of freshwater for drinking, domestic, agricultural, and industrial purposes. Pure and highquality water is an essential necessity for the sustainability of healthy life, food security, the ecosystem, and socioeconomic growth and development. It is, therefore, important to always preserve and protect the quality of this natural resource. However, studies have shown that the quality of groundwater largely depends on land use (Reddy et al. 2018; Florea 2019; Sale et al. 2019; Ukah et al. 2019), container rocks (Egbueri 2019a, b, c; Egbueri et al. 2019; Mgbenu and Egbueri 2019; Raphael et al. 2018; Shakerkhatibi et al. 2019; Yetiş et al. 2019), and age (Levitt et al. 2019; Sakakibara et al. 2019). Land use is the sum of the anthropogenic factors such as domestic practices (e.g., open defecation, poor waste disposal, and sanitary practices), agriculture, mining, industrialization, and urbanization are mostly responsible for the continuous quality deterioration of available groundwater sources. Observations of groundwater quality reported from several researches have shown that most polluted groundwater is due to anthropogenic activities (Howladar et al. 2017; Selck et al. 2018; Egbueri 2018, 2019a; Ukah et al. 2018, 2019; Coyte et al. 2019; Mgbenu and Egbueri 2019; Rivera-Rodríguez et al. 2019). These activities can release loads of potentially toxic heavy metals, which can adversely affect the health of humans, aquatic lives, and the entire ecosystem, even at relatively low concentrations. The container rocks and age are rarely able to take water quality over from contamination to pollution level (Busico et al. 2018; Ismaiel et al. 2018). In other words, the contribution of geogenic processes to heavy metals contamination/pollution in groundwater is usually negligible.

Heavy metals such as Fe, Cu, Pb, Ni, Cr, and Cd have been known to be major contaminants and pollutants in water (Ravindra and Mor 2019; Wen et al. 2019; Egbueri 2020a, b). Notably, in many developing countries, a major source of these heavy metals in drinking water is industrial effluents (Ukah et al. 2018, 2019; Chinchmalatpure et al. 2019; Mahmood et al. 2019; Egbueri 2020a). In other words, it is safe to reason that most of the heavy metals found in groundwater is due to anthropogenic inputs, especially from industrial wastes. Understandably, agricultural and domestic wastes (though high in anion and cation contaminations) have almost negligible contribution to heavy metals pollution of water systems. The current study is focused on water quality data from Ajao industrial zone in Lagos, southwestern Nigeria. This industrial area is known to have some contaminated drinking water sources (Ukah et al. 2018). This is evident from the distasteful, colored, and mal-odorous water often obtained from some hand-dug wells and boreholes in some parts of the area. In order to further ascertain and reestablish the fitness of the drinking water supplies for human consumption, the groundwater quality assessment using a unique and unbiased numerical model is therefore necessary in the area.

In the southwestern part of Nigeria, different numerical models, such as water quality index (WQI), have been used in several groundwater quality assessments. In the Ajao area, Ukah et al. (2018, 2019) recently assessed the groundwater quality based on integrated physicochemical and microbiological techniques. Their research found that the concentrations of some of the analyzed heavy metals were above the recommended limits for safe consumption. However, no known previous study in this region utilized entropy-weighted water quality index (EWQI). Although WQI seems to be the most widely used numerical model for water quality assessment, the analysis it provides is usually dependent on the accuracy of expert judgment, because the weighted factor is only determined by expert discretion (Li et al. 2010; Amiri et al. 2014). This usually introduces bias in water quality analysis. Moreover, other indexical and numerical methods employed in water quality assessments have the limitation of exclusivity to some selected parameters. However, this is not the same case with EWQI. Presently, the EWQI is a model that is believed to provide the most unbiased, justifiable, accurate, and reliable analysis of groundwater quality (Li et al. 2010; Wu et al. 2011; Amiri et al. 2014; Feng et al. 2019; Singh et al. 2019; Subba Rao et al. 2019; Wang et al. 2019). Therefore, in this study, the EWQI model is utilized in the investigation of the groundwater quality in Ajao industrial area, Lagos, Nigeria. Water quality data analyzed in March-April 2016 were used for this study. The current study is believed to be the first to use the EWQI model for groundwater quality assessment in the southwestern Nigeria. Specifically, the major aim of this study is to assess the effect of heavy metals on the quality and suitability of the groundwater in Ajao industrial area for drinking purposes using environmental pollution risk assessment tools, the EWQI, and hierarchical cluster analysis (HCA). Moreover, this paper seeks to provide an answer to the hypothesis that there may be alternative sources (other than industrial effluents) of the heavy metal pollutants in the groundwater.

Background of the study area

Location and activities

The Ajao area is in Oshodi-Isolo Local Government Area (LGA) of Lagos State, Nigeria. It is located within latitudes 6° 31' to 6° 33' N and longitudes 3° 18' to 3° 20' E (Fig. 1). The area covered in this study is relatively a small industrial estate with huge population (estimated to be around 500,000 residents), whose major source of water is underground water. In this area, there are several industries and factories producing various consumer products. Many of these industries and factories produce both solid and fluidal wastes, which are often released into flowing streams and on bare ground surfaces. Currently, it is not certain how/ whether these factories treat their industrial wastewaters before releasing them into the environment. In general, it is believed that the high level of industrial activities and wastes generated in this area expose the available drinking water resources to heavy metals contamination and pollution.

Climate, geology, and hydrogeology

The climate of the study region is humid-tropical. Annually, the study area experiences two seasons: a rainy season



Fig. 1 A map showing the location and geology of the study area

usually lasting from April to October and a dry season lasting from around November to March. The estimated average annual temperature is in the range of 20–32 °C, while the average annual rainfall is about 2000 mm. The major surface water bodies found in this area are the Adiyan, Ogun, and Osse rivers. These and other lagoons found in the area form the major recharge sources. Geologically, the Ajao area is underlain by two major lithologic units, the coastal plain sand and the alluvial river sand, both found within the Dahomey Basin (Omatsola and Adegoke 1981; Nwajide 2013; Ukah et al. 2018). Considering the lithology and texture, medium to poorly sorted coarsegrained sands and mudrocks intercalated with sands are predominant. In this area, the coastal plain sands form the main aquifer systems for domestic, commercial, and industrial usages (Longe et al. 1987; Ukah et al. 2019). This aquifer is usually exploited through hand-dug wells and boreholes. However, Longe et al. (1987) identified three major aquifer units of the coastal sands. According to their research, the first, second, and third aquifers can be found around depths of 35 m (6 m thick), 40-55 m (8 m thick), and 30-90 m (32 m thick), respectively. Due to their deeper depths, the second and third aquifers are the most desired sources of drinking, domestic, and industrial waters (Longe et al. 1987), as they are better insulated from surface processes that would predispose them to contamination or pollution.

Materials and methods

Sampling and measurements

The groundwater samples were collected randomly from boreholes located within the Ajao industrial area. Systematically, data that represent water that has been contaminated by industrial wastewater (i.e., those samples that were collected from the zone of influence of the wastewater) as well as some that represent water that are not contaminated by industrial wastewater were selected. In all, twenty-one (21) samples were used for this study. Prior to the field sampling, 1-L sampling plastic bottles were prewashed and sterilized. At each sampling location, the sampling bottles were rinsed using the source water to be sampled. After sample collection, each of the groundwater samples was carefully labeled, from WS01 to WS21. Of these, six (6) represent the samples with heavy metals contamination (zone of wastewater influence), while seventeen (17) are from zones with no heavy metals contamination (outside zone of wastewater influence). After the sample collection, samples were placed carefully in an ice-crested cooler to avoid atmospheric reaction prior to laboratory analysis.

pH values of the samples were determined using a Testr-2 pH meter after normalizing with buffer solution

(pH 4.7 and 9.2). The physicochemical analyses of eight heavy metals (Fe, Zn, Cu, Mn, Pb, Cd, Cr, and Ni) were analyzed for each sample using specific hollow cathode lamp at a specific wavelength, and then aspirated into the flame of atomic absorption spectrophotometer (AAS, PerkinElmer Analyst 200). For total dissolved solids (TDS), all the samples were standardized with 342 ppm sodium chloride calibration solution and then measured with portable combined electrical conductivity/TDS/ temperature meter (HM Digital COM-100). The chloride concentrations were measured by argentometric titrimetric method, after titrating aliquot portion of water samples with a standard solution of silver nitrate solution using potassium chromate as an indicator.

All data analyses were computed using the standard limits of Standard Organization of Nigeria (SON 2015) and World Health Organization (WHO 2017).

Environmental pollution risk assessment

Geoaccumulation index (I_{aeo})

Although the I_{geo} model was initially developed for soil quality studies (Müller 1969), it has also been widely used by researchers in the assessment of the level of heavy metals pollution in drinking water (Bhutiani et al. 2017). The eight heavy metals analyzed in this study were utilized in the I_{geo} analysis. The I_{geo} model is defined by Eq. 1.

$$I_{\text{geo}} = \log_2 \frac{C_{\text{HMS}}}{1.5 \times \text{GBV}},\tag{1}$$

where $C_{\rm HMS}$ is the concentration of heavy metals in soils; GBV is the geochemical background value (i.e., the WHO standard limits). The constant 1.5 allows to analyze natural fluctuations in the content of a given substance in the environment (Müller 1969; Bhutiani et al. 2017; Adimalla and Wang 2018). Classifications of water quality based on the $I_{\rm geo}$ are as follows: uncontaminated ($I_{\rm geo} \leq 0$); uncontaminated to moderately contaminated ($0 < I_{\rm geo} \leq 1$); moderately contaminated ($1 < I_{\rm geo} \leq 2$); heavily contaminated ($3 < I_{\rm geo} \leq 4$); heavily to extremely contaminated ($4 < I_{\rm geo} \leq 5$); and extremely contaminated ($I_{\rm geo} \geq 5$) (Muller 1969; Bhutiani et al. 2017; Adimalla and Wang 2018).

Enrichment factor (EF)

Similar to the geoaccumulation index (I_{geo}) , the enrichment factor (EF) is an environmental pollution risk assessment tool (model) used in investigating the extent of heavy metals enrichment in water and sediments. In this study, the EF model was employed to further analyze the extent

of heavy metals contamination and pollution in the drinking water resources of Ajao industrial area. The EF evaluation was carried out using Eq. 2.

$$CF = \frac{C_{\rm s}}{C_{\rm ref}} \bigg/ \frac{X_{\rm b}}{X_{\rm ref}},\tag{2}$$

where C_s is the concentration of metals in the sample; C_{ref} is the concentration of reference metal in the sample; X_b is the background metal; X_{ref} is the reference background metals. The mean value for each heavy metal was used as the background metal. EF results will be classified as follows: Negligible to minimal enrichment (EF < 2); Moderate enrichment (EF = 2–5); Significant enrichment (EF = 5–20); Very high enrichment (EF = 20–40); Extremely high enrichment (EF > 40) (Loska et al. 2004; Adimalla et al. 2019).

Vector modulus of pollution index (Pl_{vector})

Vector modulus of pollution index (PI_{vector}) was proposed by Gong et al. (2008), for the determination of the extent of heavy metals pollution. This model has been successfully used by several authors (Kowalska et al. 2018). The PI_{vector} was calculated for all the samples using Eq. 3.

$$\mathrm{PI}_{\mathrm{vector}} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} \mathrm{PI}^2}$$
(3)

$$PI = \frac{Concentration of heavy metal in sample}{Corresponding WHO standard limit of heavy metal},$$
(4)

where *n* is the number of determined heavy metals; PI is the calculated value for single pollution index as given in Eq. 4 (Inhaber 1974; Cai et al. 2015; Kowalska et al. 2018; Egbueri 2019c). Classification of samples based on the PI_{vector} is as follows: low pollution ($PI_{vector} < 1$); moderate pollution ($\leq 1 PI_{vector} < 3$); considerable pollution (≤ 3 $PI_{vector} < 6$); and very high pollution ($PI_{vector} \geq 6$) (Cai et al. 2015).

Entropy water quality index (EWQI)

The enhanced water quality index of both group of samples was computed to determine the drinking quality of water. This index provides an unbiased measure of water quality considering all the measured parameters for each water sample. A five-step approach was used to compute the EWQI as given by Li et al. (2010). Firstly, we determined the information entropy (ej) as follows:

$$ej = -\frac{1}{\ln n} \sum_{i=1}^{z} Pij \ln Pij,$$
(5)

where n is the total number of samples and *Pij* denotes the probability of occurrence of the normalized value of the parameter *j* expressed as

$$Pij = \frac{Pij}{\sum Pij}.$$
(6)

Assuming there are *y* samples of water (i=1, 2, 3...z) on which *x* number of parameters (j=1, 2, 3...n) are to be tested to measure the quality of the water, matrix of such distribution will be given as

$$\mathbf{X} = \begin{vmatrix} x_{11} & x_{12} & \cdots & x_{1n} \\ x_{21} & x_{22} & \cdots & x_{2n} \\ & & \vdots \\ x_{z1} & x_{z2} & \cdots & x_{zn} \end{vmatrix}$$
(7)

Upon transformation, the Y matrix becomes

$$\mathbf{Y} = \begin{vmatrix} y_{11} & y_{12} & \cdots & y_{1n} \\ y_{21} & y_{22} & \cdots & y_{2n} \\ & & & \vdots \\ y_{z1} & y_{z2} & \cdots & y_{zn} \end{vmatrix}$$
(8)

Thus, the ratio of index values of *j* and *i* in the sample is given by

$$Pij = \frac{yij}{\sum_{i=1}^{z} yij}.$$
(9)

The second step is to calculate the entropy weight of each parameter (w_i) :

$$wj = \frac{1 - ej}{\sum_{j=1}^{n} (1 - ej)}.$$
(10)

The quality rating scale (qj) for each parameter in every sample is calculated using the formula

$$qj = \frac{Cj}{Sj} \times 100,\tag{11}$$

where C_j is the concentration of parameters in each water sample in mg/l and S_j is the measured standard of each parameter in water samples in mg/l as given by SON (2015) except where other standard is quoted.

Finally, the entropy (enhanced/improved) water quality index (EWQI) is calculated as

$$EWQI = \sum_{j=1}^{n} wj \times qj$$
(12)

Categorization of heavy metals for EWQI data analysis

Heavy metals measured in this study include Fe, Zn, Pb, Cu, Ni, Cr, Mn, and Cd. These metals were divided into two groups. The first group comprises of those that are ubiquitous in all the samples (herein called background heavy metals), and the second group are those that are exclusive to the water sampled from wastewater zone of influence (herein called anomalous heavy metals). The background heavy metals include Fe, Zn, and Cu while Pb, Ni, Cr, Mn, and Cd belong to the anomalous heavy metals group. Aside sparsity used in separating anomalous heavy metals from background heavy metals, the authors considered concentration level and health hazard potential in classifying these metals. This approach allows us to idealize the extent of contamination and the potential degree of health hazard the heavy metals enriched by wastewater introduced into the water system. Except for Cu, the background heavy metals were found within safe concentrations in almost all the samples and are metals with no known carcinogenic health effects to humans (Ukah et al. 2019). The low concentrations of the background heavy metals Fe and Zn suggest that their enrichment could possibly be chiefly controlled by geogenic processes. However, the anomalous heavy metals are peculiarly attributed to anthropogenic inputs (wastewaters).

The background heavy metals were used in computing the EWQI for all the samples. This is because they were found to be in all the samples, indicating that they may not have been introduced by the wastewater. On the other hand, the EWQI of all the samples with anomalous heavy metals was computed using both background and anomalous heavy metals. This method was designed to clearly alienate and show the effect of the anomalous heavy metals on the computed EWQI (water quality) by providing an equal and clear cutoff for heavy metals that are exclusively from wastewaters. This is similar to the factor analysis study done by Busico et al. (2018).

Results and discussion

Physicochemical characteristics of the groundwater

Results of the physicochemical analysis of all the samples are presented in Table 1. pH ranged from 5.1 to 6.9. The recommended pH for drinking water is 6.5–8.5. It was noticed that about 61% of the analyzed samples are slightly more acidic than recommended. This could be reflecting the activity of the water in dissolving metals. None of the samples was found to be overly enriched in hydroxonium ion. Excess acidity is not known to cause any direct health hazard aside its reactivity with metals and pipes. Total dissolved solids (TDS) is a measure of dissolved materials in

Table 1 Physicoch	emical charac	teristics of the g	rroundwater fro	om Ajao industrial	area						
Sample number	Hd	Measured in r	ng/l								
		TDS	CI	Fe	Zn	Pb	Cu	Ni	Cr	Mn	Cd
WS01	6.68	37.70	11.00	0.043	0.443	I	0.514	. 1	1	. 1	I
WS02	5.30	37.10	28.00	0.045	0.051	I	0.362	I	I	I	I
WS03	6.60	27.30	12.00	0.052	0.214	I	0.062	I	I	I	I
WS04	5.50	57.50	24.00	0.063	0.217	I	0.059	Ι	I	Ι	Ι
WS05	5.90	134.00	16.00	0.043	0.319	I	0.044	I	I	I	I
WS06	6.40	121.00	16.00	1.502	1.660	0.002	1.023	0.730	0.320	0.130	0.003
WS07	5.86	156.00	12.00	0.057	0.343	I	0.412	I	I	I	I
WS08	5.52	95.80	20.00	0.752	0.963	I	0.651	I	I	0.003	I
WS09	6.67	108.00	12.20	0.054	0.493	I	0.043	I	I	I	I
WS10	5.22	255.00	32.00	0.049	1.563	I	0.162	I	I	I	I
WS11	5.10	88.30	16.00	0.049	0.912	I	0.066	I	I	I	I
WS12	5.72	60.00	20.00	1.742	0.883	0.021	2.261	0.053	0.220	0.016	0.005
WS13	5.67	51.40	12.00	0.072	1.003	I	0.315	Ι	I	I	I
WS14	6.90	11.50	24.00	0.052	0.394	I	0.062	I	I	I	Ι
WS15	5.46	285.00	40.00	1.630	1.732	0.013	3.142	0.033	0.130	0.023	0.003
WS16	5.40	47.00	12.00	0.813	0.323	I	Ι	0.001	0.002	Ι	Ι
WS17	5.53	50.80	12.00	0.061	0.912	I	0.210	Ι	I	Ι	Ι
WS18	6.62	41.40	28.00	0.043	0.763	I	0.713	Ι	I	Ι	Ι
WS19	5.52	54.40	12.00	0.039	0.573	I	0.664	I	0.003	I	I
WS20	5.71	18.80	44.00	0.066	0.445	I	0.637	Ι	I	Ι	Ι
WS21	6.90	31.50	20.000	0.056	0.883	I	0.072	Ι	I	Ι	Ι
Range	5.1 - 6.9	11.5–285	11-44	0.039 - 1.742	0.051-1.73	0.00 - 0.021	0.00-3.142	0.00-0.73	0.00 - 0.32	0.00 - 0.13	0.00 - 0.005
Average	5.9133	84.2619	20.1524	0.3468	0.7185	0.0017	0.5464	0.0389	0.0321	0.0082	0.0005
SD	0.5946	73.0590	9.6264	0.5785	0.4814	0.0053	0.7842	0.1589	0.0854	0.0285	0.0014
SON (2015)	6.5-8.5	500	250	0.3	6	0.01	1.0	0.02	0.05	0.2	0.003
WHO (2017)	6.5-8.5	600-1000	200–300	0.3	4	0.01	0.05	0.07	0.05	0.4	0.003
SD standard deviat	ion										

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the water (Egbueri 2019a). The TDS was found to range from 11.5 to 285 mg/l with a mean of 84.26. The TDS of all the water samples were below the recommended limit of 500 to 1000 mg/l. Usually, TDS affect the acidity, turbidity, and salinity of water. Water with high TDS is commonly known to have undesirable color, taste, and odor. It is the major determinant of the appearance of water as well as the chemical status of the water. No health effect is directly linked to TDS except for the undesirable influence it has on other properties of the water.

The acceptable limit for chlorine in drinking water is set at 250 mg/l. Excess of Cl impacts on the fresh taste of water. The analyzed chlorine ranges from 11 to 44 mg/l with a mean value of 20.15 mg/l. About 24% of the total samples were found to be above the recommended limit of 0.3 for Fe^{2+} in drinking water. The range of Fe^{2+} was found to be 0.039-1.74 mg/l, averaging at 0.7185 mg/l. 'Red hot disease' has been reported to be an adverse consequence of ingesting Fe-contaminated water (Ukah et al. 2019; Egbueri 2019c). Zn^{2+} was found to range from 0.051 to 1.73 mg/l. All the samples are much lower than the set limit of 3 mg/l. Health effects of Pb²⁺ to human include carcinogenic potential, interference with mental development, and the central and peripheral nervous system (SON 2015; Ukah et al. 2019; Egbueri 2020a, b). The adverse health effect of Pb^{2+} could be so bad that only 0.01 mg/l is allowable. Pb²⁺ was not detected in about 86% of the samples. Only three samples reported high Pb²⁺ enrichment. Of the three samples, two were above the threshold with a range of 0.00-0.021 mg/l and an average of 0.017 mg/l (Table 1).

One of the water samples did not contain Cu. However, about 14% of the samples were above the limit of 1 mg/l (Table 1). Cu concentrations ranged from 0.00 to 3.142 mg/l with an average of 0.55 mg/l. SON (2015) reported that excessive Cu in drinking water could lead to gastrointestinal problems. Moreover, excess Cu can also lead to liver damage and kidney disease (Ukah et al. 2019; Egbueri 2020a). Nickel was detected in only four samples. Three of these four samples had concentrations over the recommended limit of 0.02 mg/l. The range is from 0.00 to 0.73 mg/l and an average of 0.038 mg/l. Nickel is known to be carcinogenic. Cr^{3+} was detected in only five of the samples. Allowable limit of Cr^{3+} is 0.05 mg/l as it is cancerous. Three of the five samples were found to be above the limit. The range of Cr is 0.00-0.32 mg/l with an average of 0.032 mg/l. Of the four samples that reported Mn²⁺ enrichment, one was found to be above the limit of 0.2 mg/l with a range of 0.00-0.23 mg/l and an average of 0.0082 mg/l. Mn²⁺ is known to cause neurological disorder (SON 2015; WHO 2017; Mgbenu and Egbueri 2019). Cd²⁺ was detected in only three samples and all are at levels at or above the threshold of 0.003 mg/l. Studies have shown that excess Cd²⁺ in drinking water could lead to anemia, renal stone formation, bronchitis, and kidney

problems (SON 2015; WHO 2017; Ukah et al. 2019). With an average of 0.005 mg/l, the concentration ranged from 0.00 to 0.005 mg/l. Pb, Ni, Cr, Mn, and Cd are considered as anomalous heavy metals in this study as their enrichment is traceable to industrial effluents.

Environmental pollution risk assessment

Geoaccumulation index (I_{qeo})

For the geoaccumulation index (I_{geo}) , the order of increase in contamination rate of the analyzed heavy metals is Zn> Cu>Fe>Ni>Cr>Mn>Pb>Cd. Table 2 presents a summary of the I_{geo} analysis for the twenty-one (21) groundwater samples. Based on the classification stated earlier in the methodology section, about 66% of the total samples were in uncontaminated to moderately contaminated categories. This indicates that they have not been heavily loaded with the heavy metals. However, about 19% showed moderate to heavy contamination, whereas 14.28% (samples WS06, WS12, and WS15) are heavily contaminated with heavy metals.

Enrichment factor (EF)

This study has revealed that all the analyzed groundwater samples are variedly enriched with heavy metals. Table 2

Table 2	Environmental	pollution	indices
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Sample number	$I_{\rm geo}$	EF	PI _{vector}
WS01	1.856255	1.7	8.2E-01
WS02	1.336093	0.9	6.9E-01
WS03	- 0.79475	0.6	3.3E-01
WS04	-0.78201	0.6	3.3E-01
WS05	- 1.12099	0.7	2.9E-01
WS06	4.213088	60	7.568
WS07	1.560498	1.4	7.4E-01
WS08	2.640415	5.1	1.1691
WS09	- 0.95394	1.0	3.1E-01
WS10	0.619387	2.6	5.4E-01
WS11	- 0.41205	1.5	3.8E-01
WS12	4.491896	42	4.951
WS13	1.31202	2.2	6.8E-01
WS14	- 0.69796	0.8	3.4E-01
WS15	4.712412	34	5.512
WS16	0.924818	2.9	6.0E-01
WS17	0.797613	1.8	5.7E-01
WS18	2.32724	2.5	5.7E-01
WS19	2.226714	2.2	9.4E-01
WS20	2.167429	2.0	9.2E-01
WS21	- 0.32073	1.5	3.9E-01

shows that 11 samples (52%) have minimal enrichment, 7 samples (33%) are moderately enriched, while 3 samples (WS06, WS12, and WS15) have extremely high enrichment. These three sample are believed to be those that received higher impacts of the industrial effluents. In other words, their very high EF values are indicative of the excessive effluents' imprints.

Vector modulus of pollution index (PI_{vector})

The results of the PI_{vector} evaluation are summarized in Table 2. It was observed that 17 groundwater samples (80.9%) have low pollution. However, one sample (WS08) has a PI_{vector} value greater than 1 but less than 3, indicating a moderate pollution. Beside, three samples (WS06, WS12, and WS15) have considerable to very high pollution.

Entropy water quality index (EWQI)

Table 3 presents the entropy weight (wj) and information entropy (ei) of all the analyzed water quality parameters. Meanwhile, Table 4 shows the obtained quality ratings of the parameters per the groundwater samples. The final EWQI results show that all of the samples collected from areas outside the zone of the wastewater influence are of excellent water quality (Table 5). The groundwater quality in the study area was classified using the EWQI classification scheme whereby EWQI < 50 (Rank 1, Excellent water quality); 50-100 (Rank 2, Good water quality); 100-150 (Rank 3, Average water quality); 150-200 (Rank 4, Poor water quality); and > 200 (Rank 5, Extremely poor water quality) (Li et al. 2010; Wu et al. 2011; Amiri et al. 2014; Singh et al. 2019; Feng et al. 2019). Of the six water samples collected within the zone of influence of the wastewater, two were of extremely poor water quality, one was of poor water quality, and three were found to be of excellent water quality (Table 5). These three were found to be in the second quartile of the EWQI range for that class and constituted the upper range of all the measured samples that were found to be of excellent water quality. This simply means that the quality of the samples may be actively deteriorating. Again, it is important to note that these samples were collected much farther into the zone of influence of industrial wastewater and are considerably sparse in heavy metals concentration. WS16 had no detected Pb, Cu, Mn, and Cd. WS19 had no detected Pb, Ni, Cr, Mn, and Cd, while WS8 had no detected Pb, Ni, Cr, and Cd. We consider that the intermittence in the presence of these heavy metals in this set of samples is a function of the increasing distance within the zone of influence and is the reason for the excellent quality of the water as compared to the others where all the heavy metals were detected.

able 3 Entr	opy weight (wj)	and information	entropy (ej)								
arameter	Hq	TDS	CI	Fe	Zn	Pb	Cu	Ni	Cr	Mn	Cd
vj	0.0006323	0.0432009	- 0.008539	0.0641809	0.03060974	0.1029334	0.1030848	0.3094112	0.1459878	0.1957994	0.0126985
j	0.9985694	0.9022607	1.019319	0.854795	0.93074749	0.7671201	0.7667774	0.2999777	0.6697122	0.5570169	0.9712706

Table 4 Qual	ity rating (qj) of	the parameters p	er water samples								
Parameter	ЬH	TDS	CI	Fe	Zn	Pb	Cu	Ni	Cr	Mn	Cd
WS01	0.049693	0.3257351	-0.0375717	0.919926	0.4520038	1	5.2985606	I	I	1	I
WS02	0.0394271	0.3205509	-0.0956372	0.9627132	0.0520366	I	3.7316711	I	I	I	I
WS03	0.0490979	0.2358771	-0.0409874	1.1124686	0.2183495	I	0.639126	I	I	Ι	I
WS04	0.0409149	0.4968108	-0.0819747	1.3477985	0.2214104	Ι	0.6082005	I	I	I	I
WS05	0.0438905	1.1577851	- 0.0546498	0.919926	0.3254836	I	0.4535733	I	I	I	I
WS06	0.0476101	1.0454626	- 0.0546498	32.133229	1.6937389	2.0586672	10.545579	1129.3508	93.4322	12.726959	1.269847
WS07	0.043593	1.3478692	-0.0409874	1.2194368	0.3499713	Ι	4.2470953	I	I	Ι	I
WS08	0.0410637	0.8277299	-0.0683123	16.088008	0.9825726	I	6.7108229	I	I	0.2936991	I
WS09	0.0496186	0.9331402	-0.0416705	1.1552559	0.50302	I	0.4432648	I	I	I	I
WS10	0.038832	2.2032477	-0.1092996	1.0482878	1.5947674	Ι	1.6699744	I	I	Ι	I
WS11	0.0379393	0.7629285	-0.0546498	1.0482878	0.9305361	I	0.6803599	I	I	I	I
WS12	0.0425515	0.5184112	-0.0683123	37.267699	0.9009467	21.616005	23.307482	81.993959	64.234637	1.5663949	2.1164117
WS13	0.0421796	0.4441056	-0.0409874	1.5403412	1.0233856	I	3.2471724	I	I	I	I
WS14	0.0513296	0.0993622	-0.0819747	1.1124686	0.4020079	Ι	0.639126	I	I	I	I
WS15	0.0406173	2.4624533	-0.1366245	34.871613	1.7672023	13.381337	32.389256	51.052842	37.956831	2.2516927	1.269847
WS16	0.040171	0.4060888	-0.0409874	17.393019	0.3295649	I	I	1.5470558	0.5839513	I	I
WS17	0.0411381	0.4389215	-0.0409874	1.3050113	0.9305361	Ι	2.1647816	Ι	Ι	Ι	I
WS18	0.0492467	0.3577037	-0.0956372	0.919926	0.7785077	I	7.3499489	Ι	I	I	I
WS19	0.0410637	0.4700262	-0.0409874	0.8343515	0.584646	Ι	6.8448332	Ι	0.8759269	Ι	I
WS20	0.0424771	0.1624355	-0.150287	1.4119794	0.4540445	Ι	6.5665042	Ι	Ι	Ι	I
WS21	0.0513296	0.2721659	- 0.0683123	1.1980431	0.9009467	I	0.7422108	I	I	I	I

Table 5	EWQI (computed	d from a	ll the me	sasured p	arameters															
Sample	WS1	WS2	WS3	WS4	WS5	WS6	WS7	WS8	6SM	WS10	WS11	WS12	WS13	WS14	WS15	WS16	WS17	WS18	WS19	WS20	WS21
EWQI	7.0	5.0	2.2	2.6	2.8	1284.2	7.2	24.9	3.0	6.4	3.4	233.5	6.3	2.2	177.3	20.3	4.8	9.4	9.6	8.5	3.1
Rank	1	1	1	1	1	5	-	1	1	1	1	5	1	1	4	1	1	1	1	1	1

Figure 2 presents a comparison of the EWQI for the six samples collected from the zone of influence of the industrial wastewaters. The EWQIs shown in this figure were computed from different parametric sizes representing different contamination scenarios. This was done in order to answer the question of whether the industrial wastewater was responsible for the poor water quality observed in the area or to determine the extent of contamination due to the effluentderived heavy metals. The capacity of the heavy metals to contaminate groundwater can also be seen from this figure. In the first EQWI (in blue), we used all the measured parameters to calculate the EWQI. This represents the true state of the quality of water as at the time of this investigation and by this, 50% of the water were at or worse than poor quality. The other 50% were of excellent quality but were seen as fast deteriorating. The second EWQI (in brown) were computed without the contributions of the anomalous heavy metals. This was done to be able to idealize what the EQWI would be without the contribution of the anomalous heavy metals. From this, we found that the quality of WS06 was greatly affected by the anomalous heavy metals as the quality of this water would be poor (EWOI of 195.8) instead of extremely poor (EWQI of 1284.2). Expectedly, this sample was taken very closely to the waste water dislodging point. The other five samples showed trend against expectation. The quality of waters was seen to relatively worsen slightly when the contribution of the anomalous heavy metals was removed (Fig. 2). We strongly consider this to be due to the uncertainty in processing stochastic data such as this one. Without the contributions of the anomalous heavy metals in the computation, the other parameters assumed larger proportion of entropy weight (wj) that bulks up the EWQI. However, this gives a great picture of how these anomalous heavy metals can potentially cause offsets to water quality.

To show the general capacity of heavy metals to affect the quality of water in this study area, we compared the EWQI (in blue) to the EWQI (in gray). The difference between the two is the total effect of the heavy metals to water quality. The EWQI (in gray) was computed without all of the heavy metals (Both background and anomalous heavy metal). This is with the assumption that the water does not contain heavy metals. We thus showed what the EWQI would be without any of the heavy metals. Our result showed that all the six water samples collected from the zone of influence of the wastewater would be of excellent quality, except for WS15 whose quality was measured as good. Summarily, the presence of the heavy metals moved the water pollution level from excellent quality to poor quality.

From this study, it can be seen that heavy metals have the potential to cause great offset in the quality of water. A similar finding has been reported by Boateng et al. (2019). In Ajao area, it has been established that industrial effluents contain heavy metals (Ukah et al. 2018) and these heavy





metals have been traced to be present in groundwater and causes different levels of contamination depending on proximity to the point source and environmental conditions. It cannot be conclusively said that the heavy metals from the industrial effluent is solely responsible for the poor water condition in the area. This is because the EWQI computed without the anomalous metals compared to the EWQI calculated from the total parameters do not support that hypothesis. We expect the EWQI computed without the anomalous metals to improve considerably against the EWQI computed from the total parameters for us to be able to say that the heavy metals are responsible for the poor water quality. Only one of six samples followed this expectation. This study examined wastewater collected from one of the factories only and analyzed for chemicals related to the business of that factory. It is likely that the other contributors to the poor water quality in the area are coming from other industrial processes and other anthropogenic sources as well.

Water quality clustering

The results of the three environmental pollution assessment tools (I_{geo} , EF, and PI_{vector}) were integrated with the EWQI results to obtain a final overview of the water quality in the Ajao industrial area. HCA was performed on these results. The HCA was carried out using SPSS software (v. 22). The Ward's linkage method (with squared Euclidean distance and z-score standardization) was utilized to produce a dendrogram (Fig. 3) demarcating the quality of the groundwater samples. The standardization of the data was to remove bias due to the differences in the values of the four models. Result of the HCA (Fig. 3)

shows that all the samples fall into two major quality groups. Although Cluster 1 has two sub-clusters, it is mainly comprised of those samples with minimal heavy metals contamination and all were identified by the EWQI as excellent drinking water. On the other hand, Cluster 2 is comprised of those three samples (WS12, WS15, and WS06) heavily loaded with heavy metals. These samples are marked unsuitable for human consumption.

Conclusions

This paper has presented a case study of the application of EWQI in assessing the effect of effluent-derived heavy metals on the groundwater quality in Ajao industrial estate, Nigeria. The I_{geo} , EF, PI_{vector}, and the EWQI have proven to be efficient in the assessment of pollution status and suitability of drinking water. It was found that the majority (85.71%) of the analyzed groundwater samples are in excellent condition for drinking, while 14.29% are very unsuitable for human consumption. Based on the findings of this paper, it is concluded that the heavy metals from the effluents of the area sampled contribute significantly to the poor quality of underground water in Ajao estate, but it is certainly not the only source. There could also be other possible sources (contributors) to this problem. Therefore, it is necessary to look at other sources of pollutants in the area. This study also revealed that heavy metals have great capacity to negatively affect groundwater quality and as such, efforts must be made to ensure maximum protection of the groundwater system in the Ajao industrial area.





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Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests.

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