Available online at http://www.ajol.info/index.php/njbas/index
Nigerian Journal of Basic and Applied Sciences (June, 2022), 30(1): 05-23
DOI: http://dx.doi.org/10.4314/njbas.v30i1.2
ISSN 0794-5698

Full Length Research Article

Cadmium Geochemistry and Groundwater pollution Status Evaluation using Indexing and Spatial Analysis for Keffe Community and Environs Sokoto Basin, North Western Nigeria

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ABSTRACT

Representative groundwater samples were collected from the Kaffe community and environs to evaluate the concentrations and geochemical constraints for mobilizing cadmium (Cd) and selected heavy metals. Field-based *in-situ* measurements of physicochemical parameters were combined with Atomic Absorption Spectrophotometer analysis of dissolved elemental concentrations. Pollution indices (i.e. heavy metal pollution index; HPI, heavy metal evaluation index; HEI, contamination degree; Cd, metal index; MI, synthetic pollution index; SPI, ecological risk index; ERI and Nemerow index; NI) evaluations highlighted the levels of heavy metals in the groundwater. Cadmium and iron (Fe) concentrations exceeded the recommended limits in 97% of the analysed samples, with an average pH of 6.3. Strong positive correlations were observed between cadmium and the computed pollution indices (p 0.774 to p 0.100), suggesting significant Cd pollution of the groundwater. Components analysis grouped Cd, Fe, and the pollution indices in the first PC. This was favourably compared to the correlation analysis result. Cluster analysis categorized Cd, Zn and pH in the first cluster consistent with the suggested dissolution and enrichment of Cd and Zn in the groundwater under similar geochemical conditions. The study area is medium and moderately polluted based on HPI, HEI, Cd, and NI.

Keywords: Cadmium toxicity; Pollution indices, multivariate statistics; groundwater contamination; Cadmium mobility.

INTRODUCTION

Kaffe community, like most agrarian settlements, overly depend on groundwater for domestic uses, accessed through boreholes, tube and hand-dug wells. The semi-arid location of these communities couple to other factors that include Sahel savannah climate, the erratic and shortraining season been experience in this area andover-exploitaion of groundwater, has resulted in observable changes in water quality, with consequent increase in health risks. The quality of groundwater is influenced by both natural and anthropogenic processes and activities. Geology, geochemical and environmental factors, including rock porosity and permeability, element mobility and ion exchange, rainfall, temperature, and pH conditions are the major determinants of natural and suitability of groundwater for domestic and other uses.

Highly toxic elements, including mercury, lead, arsenic and cadmium have been established as dangerous groundwater pollutants and pose constant health risks, especially in rural communities that directly utilize such (Burke, 2016).

Geochemically, trace elements are chemical elements whose concentration in the Earth's crust is less than 0.1 % by weight (Navrátil and Minařík, 2002). Cadmium occurs at low-temperature hydrothermal deposits forming sulfides, selenides, arsenate, carbonate, oxides and hydroxides. Greenockite (CdS) and otavite ($CdCO_3$) are important minerals of Cd, in association with Zn, Pb and Cu mineralization (Wedow, 1973). Cadmium minerals includes Cadmoindite ($CdIn_2S_4$), cadmoselite (CdSe), niedermayrite ($Cu_4Cd\ (SO_4)_2\ (OH)_6.4H2O$), monteporrite (CdO) and xanthocroite ($CdS.H_2O$) (Naseem, 2012).

According to Agency for Toxic Substances andDisease Registry (ATSDR, 2012) ranking, Cadmium (Cd) is the seventh most toxic heavy metal, with a crustal abundance of Cd of 0.13 $\mu g.g^{-1}$. Prolong intake of this element can result in vast and serious health problems, including renal dysfunction, osteoporosis and other lung, liver, kidney, bone and metabolic health risks (Bernard, 2008; Luparello *et al*., 2012; Jaishankar *et al*., 2014). Cadmium and its compounds are highly water-soluble compared to other metals, with standards in drinking water set at (40 lg/l) and (5 lg/l) for the short-term and long-term usage, respectively. Natural sources of Cd include rock weathering, air particles, sea spray, forest fires, volcanoes, and hydrothermal vents. Anthropogenic contributions are mainly through mining, smelting, waste disposal, fertilizers, cement, fossil fuel combustion and industrial activities (Richardson *et al*., 2001; UNEP, 2010; ATSDR, 2012, Arain *et al*., 2015). Cadmium concentrations in sedimentary rocks (0.01 to 2.6 mg/kg) are higher than those in igneous (0.07 to 0.25 mg/kg) or metamorphic rocks (0.11 to 1.0 mg/kg) (Mar and Okazaki, 2012; Smolders and Mertens, 2013). According to Six and Smolders (2014) Cd in a given soil is generally closely related toits abundance in the parent material, as well as input through atmosphericdeposition, industrial or agricultural activities

Toxic at extremely low concentrations, cadmium (Cd) has a low sorption affinity that enables easy mobilization and rapid accumulation in groundwater (Kubier *et al*., 2019). Elevated concentrations in groundwater are possible commonly through, a) geogenic release from rocks, mostly phosphate- and carbonate-bearing rocks (Smolders and Merten, 2013) with an average crustal

abundance of 0.1 – 0.2 mg/kg (UNEP, 2010). b) man-made contributions of Cd to groundwater are majorly through the application of phosphate fertilizers that contain Cd as impurities in phosphate minerals and rocks, use in the production of such fertilizers (Kubier *et al*., 2019). However the Cadmium standards in drinking water are set at (40 lg/l) and (5 lg/l) for the short-term and long-term usage, respectively.

Cadmium pollution of soils and groundwater is a global phenomenon, that substantially affects the water quality, especially in Asia and Africa (Obasi and Akudinobi, 2014; Kubier and Pichler, 2019; Aithani, 2020). Several literatures that involved the studies of Cadmium and heavy metals pollution in groundwater includes the works of Jaishankar *et al*. (2014), Arain *et al*. (2015), Adekunle *et al*. (2019), Egbueri and Unigwe (2019), Bansal (2020) Ganiyu *et al*. (2021), Karunanidhi *et al*. (2021), Hamidu (2021) and Parvin and Tareq (2021).

Several studies have been conducted on groundwater quality and general hydrogeology of Sokoto basin, recent research works include that of Hamidu *et al*. (2016). Adelana *et al*. m(2003) studied the isotope and geochemical characterization of surface and subsurface of the Sokoto basin. The authors also investigated the groundwater recharge in parts of Sokoto basin in 2006. Other similar studies were conducted by Hamidu (2017), Wali *et al*. (2020). Kogbe (1978) investigated the geochemistry of the ferruginized deposits of the Sokoto basin by measuring the concentrations of the Fe, Mn, Ni, Co, Cr, Cu, V and Ti. Studies carried out around Kaffe focused on irrigation water quality and the general hydrogeochemistry of the area (Kwaya et al., (2019a, 2019b, 2020).). However Ibrahim (2020) studied the irrigation water quality and heavy metals pollution of groudwater from Gidan Gulbi Shallow Floodplain Aquifer.

This study aim to investigate the Cadmium geochemistry and the pollution status of groundwater within Kaffe community and its environs with respect to Cadmium and other heavy metals concentrations in the groundwater and to know the sources of cadmium and factors responsible for its mobilization into the groundwater of the area.

Location, Geologic Setting and Aquifer Characteristics of the Study Area

Kaffe town and environs is located within Gada local government area of Sokoto state covering an approximate total landmass of about 800 km^2. Located within the 700, 000 km^2 Nigerian sector of the larger Iullemmeden Basin of West Africa locally referred to as Sokoto basin. Physically the study area is characterised by gentle undulating plain with isolated hilly topography the raises to about 430 metres above sea level and share border with Niger republic at it northern part. Regionally it falls within the Semi-arid zone of northwestern Nigeria and located in the Sahel savannah Climatic region of West Africa. Jones (1948) and Kogbe (1975, 1981) studied extensively the geology of the Sokoto Basin, their works revealed that Kaffe is underlain by Lower Cretaceous to Quarternary sedimentary rocks of the Sokoto Basin (Figure 1). Kaffe is underlain by Lower Cretaceous to Quarternary sedimentary rocks of the Sokoto Basin (Figure 1). Outcropping geological sequence in the study area includes units of the Rima and Sokoto Groups and overlying Gwandu Formation (Figure 1).

The eastern part of the study location is dominated by the Taloka Formation (Figure 2), the oldest Maastrichtian transgressive unit of the Rima Group. This consist of reddish-brown to white fine-grained sandstone and siltstone, with beds of shale and mudstone. Overlying this unit and occupying the northeastern portion of the study, is the Dukamaje Formation with the type locality located in the study area. Dark grey fossiliferous shale is dominant with thin beds of limestone and mudstone. Fine-grained sandstone, siltstone and intercalated mudstone are observed in the central part of the study area, stretching from Gada, through Kaffe to Karangiya settlements. These units are of the Wurno Formation that forms the uppermost sequence of the Rima Group. The overlying Paleocene units consist of the phosphate nodule-bearing shale and yellowish-brown limestone of the Dange Formation. In the southwestern part of the study area, white crystalline and interlocking limestone of Kalambaina Formation were observed together with brown shale. Groundwater in the study area is confined in aquiferous zones of fine to coarse sandy units, porous karstic limestone, and the overlying regoliths (Anderson and Ogilbee 1973; Bassey *et al*., 1999; Adelana *et al.,* 2002; Yelwa *et al*., 2018).

METHODOLOGY

Sampling and Analysis

To assess the Cd concentrations in the groundwater, thirty (30) groundwater samples were collected in polyethene bottles from boreholes and hand-dug wells, after rinsing three times with the same sampling water. The water access wells sampled were all currently being utilized, by the local communities for domestic uses as at the time of sampling. Pre-sample water flow was allowed for at least 5 minutes before sampling. In-situ determination of physical parameters including temperature, pH, total dissolved solids (TDS), electrical conductivity (EC), was carried out immediately using mobile pH and temperature devices. To ensure that a greater number of metals to be analyzed were retained in solution, few mills of concentrated nitric acid solution was added. This lowered the pH of the water to about 4, consequently reducing precipitation of metallic ions out of solution.

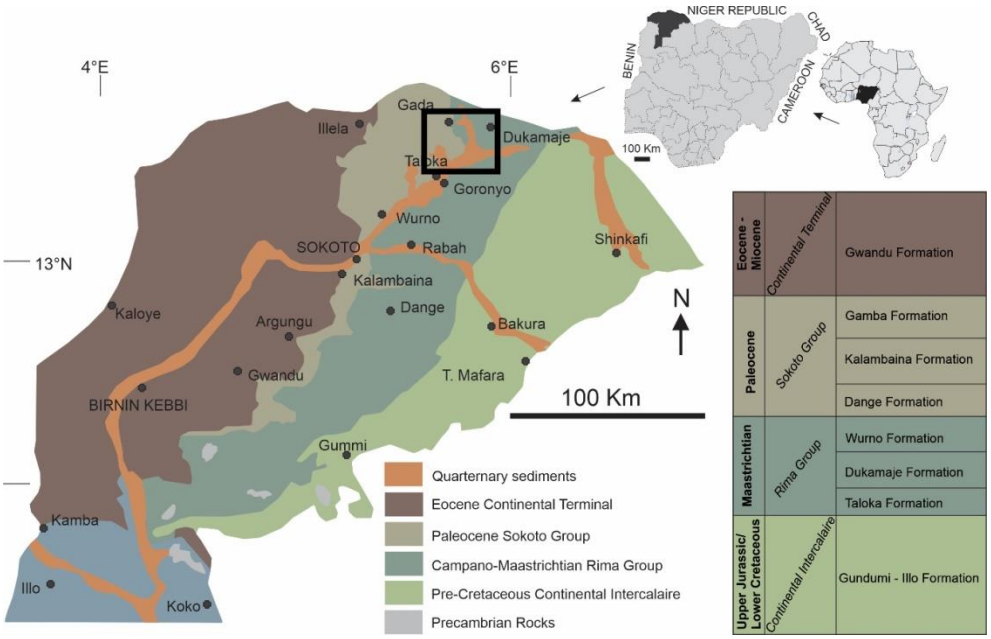

Figure 1: Simplified geological map of the Sokoto Basin. Inset maps of Africa and Nigerian highlighted for reference. Stratigraphic sequence of the Sokoto Basin shows the placement of the formations observed in the study. Black box indicates the study location (modified from Obaje, 2009)

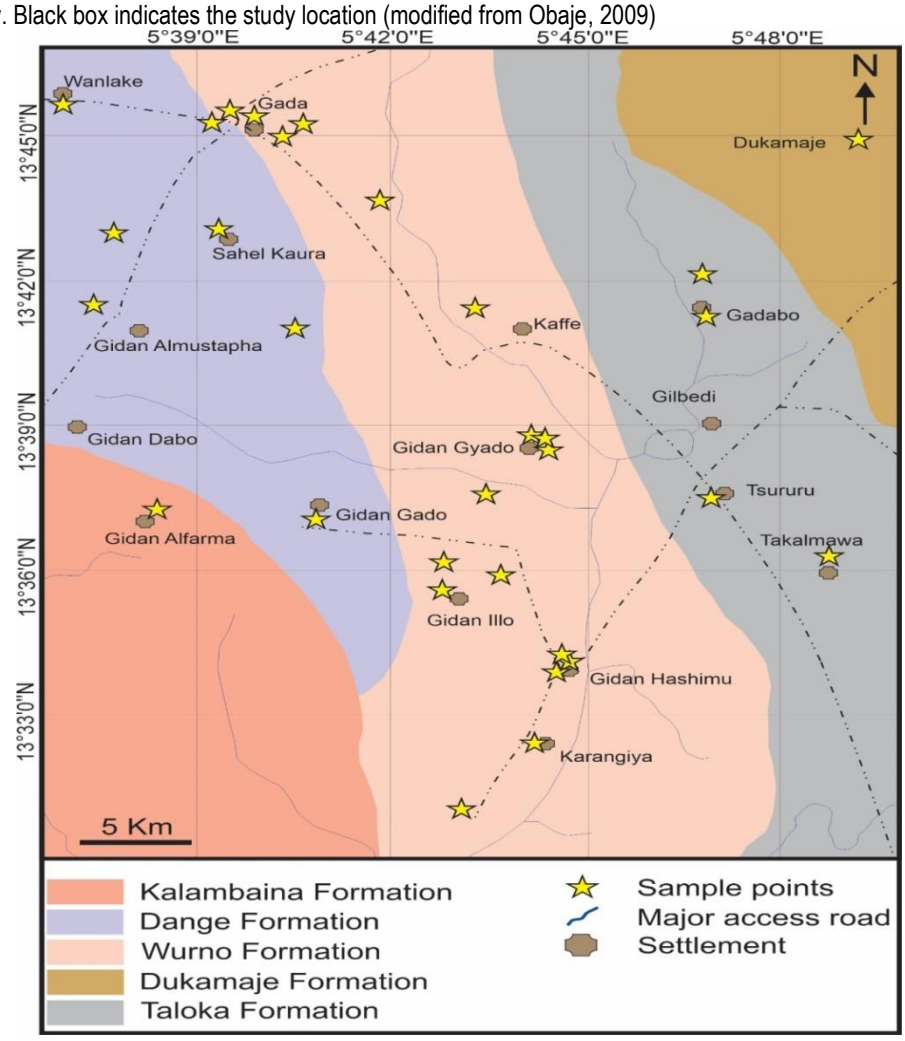

Figure 2: Geological map of the study area, indicating the distributions of the sample points and localities..

Aside Cd, other divalent cations that Cd can substitute for, due to similarities in ionic radius including Fe and Zn, were also measured. Elemental determination of dissolved trace elements was carried out by Atomic Absorption Spectrophotometer (AAS, AA 630 SCHIMADZU model) at the Biomass Instrumental Laboratory of the Centre of Energy Research, Usmanu Danfodiyo University, Sokoto, Nigeria.

Data Evaluation

Seven pollution indices, including heavy metal pollution index (HPI), heavy metal evaluation index (HEI), contamination degree (C*d*), metal index (MI), synthetic pollution index (SPI), ecological risk index (ERI) and Nemerow index (NI) were used to evaluate the levels of Cd, Fe, Mn and Zn pollution within the groundwater (Tables 1 & 2). All metals concentration are given in µg/L.

Table1: Equations used for pollution indices computation for groundwater samples collected

S/N	POLLUTION INDEX	EQUATIONS USED	MEANINSG OF SYMBOLS IN EQUATIONS	REFERENCE
1	**Heavy metal pollution index (HPI)**	$HPI = \frac{\sum_{i=1}^{n} W_i Q_i}{\sum_{i=1}^{n} W_i}$ $Q_i = \sum_{i=1}^{n} \frac{\{M_i(-)I_i\}}{(S_i - I_i)} \times 100$	Q*i* is the Sub-index of the *i*th Parameter W*i* represent the weightage of the *i*th Parameter *n* is the number of parameters been considered M*i*, I*i* and S*i* represent the Heavy metal's ith parameter monitored, ideal and standard values respectively	Mohan et al. (1996). Edet and Offiong, (2002)
2	**Contamination index (C_d)**	$C_d = \sum_{i=1}^{n} Cf_i$ $Cf_i = \frac{CA_I}{CN_i} - 1$	C*fi* is the contaminant factor for the *i-th* component C*Ai* is the analytical concentration value of the *i-th* parameter C*Ni* represent the upper permissible concentration of the *i-th* parameter N is the normative value	Tomlinson et al., (1980). Backman *et al.* (1997)
3	**Heavy Metal evaluation index (HEI)**	$HPI = \sum_{i=1}^{n} {H_c}/{H_{mac}}$	H_c is the measured concentration of i-th parameter H_{mac} the minimum admissible concentration of the *i-th* parameter.	Edet and Effiong (2002) Wagh *et al.* (2018)
4	**Synthetic Pollution index (SPI)**	$SPI = \sum_{i=1}^{n} \frac{C_i}{S_i} \times W_i \ (i = 1,2,3, \dots, n)$ $K_i = \frac{1}{\sum_{i=1}^{n} \frac{1}{Vs}}$ (*I* = 1, 2, 3 …n) $Wi = \frac{K}{Vs}$	*Ci* is concentration metal S*i* is the standard for each metal K*i*is constant of proportionality (W*i*) is weight coefficient K is the constant of proportionality Vs = standard for each of the parameters n = Total number of parameters considered Vo = observed concentration of the individual parameters	Singh *et al* (2014)
5	**Metal index (MI)**	$MI = \sum_{i=1}^{n} \frac{Ci}{(MAC)i}$	*C* is the concentration of each element MAC is the maximum allowed concentration	Tamasi and Cini (2004)
6	**Nemerow Pollution Index (NI)**	$\frac{\sqrt{\left(\frac{MCi}{SCi}\right)^2 mean + \left(\frac{MCi}{SCi}\right)^2 max}}{2}$	$\left(\frac{MCi}{SCi}\right)$mean and $\left(\frac{MSi}{SCi}\right)$max Are the average and maximum contaminant factors	Caerio et al. (2005) Liu et a*l*., (2015a)
7	**Ecological Risk Index (ERI)**	$ER \sum_{i=1}^{n} Ti \times CF$	CF is the contaminant factor of metal Ti is the potential ecological risk coefficient of a metal i.e 5 for Cu, Ni and Pb, 2 for Cr and 1 for Mn and Zn.	Håkanson, (1980) Sharifi *et al*., (2016):

Table 2: Standards used for computing pollution indices

Element	S	I	MAC	W	Wi
Cd	5	3	3	0.3	0.5
Fe	300	200	200	0.005	0.0083
Mn	100	500	50	0.02	0.025
Zn	5000	5000	5000	0.0002	0.0005
			k=	0.33	

Key: W = Weightage (1/MAC); S = Standard permissible in ppb; I = Highest permissible in ppb;
MAC = Maximum admissible concentration/upper permissible

Multivariate Statistical Analysis

The statistical data evaluation using IBM SPSS statistical package, version 21.0. was utilized to carry out the following statistical evaluation, correlation analysis (CA), principal component analysis (PCA) and Hierarchical cluster analysis (HCA), were employed to idenfy theheavy metals sources, evaluation geochemical and environmental characterization and to bring out the relation between these heavy metals.

Spatial Analysis

The inverse distance weight method (IDW) was used for the productio of the spatial maps for both the pollution indices and heavy metals concentration in the groundwater of the area by using the Arc GIS soft ware.

RESULTS AND DISCUSSION

Physicochemical Factors

Tables 3 & 4 show the physicochemical measured parameters and summary statistics of the data from this study. The temperatures and pH of the measured groundwater had mean values of 30.93 (σ 2.12) and 6.3 (σ 1.24), respectively, indicating weakly acidic groundwater. The groundwater has fewer dissolved chemical substances with an average EC and TDS of 536.03 and 260.3 mg/L.

Cadmium (Cd) concentrations in the analyzed groundwater samples vary between 3 and 47 µg/L with a mean value of 23.9 µg/L, of which 29 samples (96.7%) have Cd concentrations above the NSDWQ (2015) and WHO (2018) permissible limits of 3 µg/L (Figure 3A). The concentration level is consistent with Cd pollution, posing short and long-term health risks (Table 5). Similarly, increased health risks may arise from very high Fe concentrations (average 1057.8 µg/L) that range from 92 to 1660 µg/L (Figure 3B), exceeding the Nigerian and World health organization's permissible limits of 300 µg/L. Detectable Mn concentrations (Figure 3c) are between 9 and 1030 µg/L with a mean of 410.1 µg/L, and above the Nigerian standard for drinking water quality acceptable range limit of 200 µg/l in 25 samples (83.3%) of the samples collected, while the WHO (2018) acceptable limit of 400 µg/L was exceeded by 10 out of the analyzed samples. The average concentration value obtained indicates slightly polluted groundwater based on the WHO benchmark values. However, acceptable NSDWQ and WHO (300 µg/L) of Zn concentrations were recorded in the samples, ranging between 6 and 330 µg/L with a mean value of 65.7 µg/L (Figure 3D). The spatial distribution maps for the measured physical parameters of groundwater and detected heavy metals are displayed in Figures 3(A-H).

Pollution Characterization

Heavy metal pollution indices (HPI) range between 12 and 2050, and based on the adopted class ranges (Table 4), four of the samples are classed as low pollution, 11 samples had medium pollution, while 15 samples (50%) were highly polluted with HPI values above 1000 (Figure 4a). The study location average was 978, which placed the whole groundwater resources in the medium class of polluted water in HPI. The calculated values of HEI revealedthat 56.6 % (17 samples) of the collected groundwater samples were of medium-class while ten samples were categorized as low, and the remaining three groundwater samples were evaluated to be of high HEI (Figure 4b). The mean value for this pollution index was 12, which points to a medium polluted groundwater. C*d* values computed revealed that 12 of the sampled groundwater were highly contaminated, with the remaining 18 samples distributed between the medium and low contamination degree classes of groundwater (Figure 4c). The average value of 8.4 calculated for the whole area indicates medium contamination. The classification for MI was adopted from the work of Rezaei *et al* (2017). The values obtained fall into three out of the six categories (Figure 4d). The result revealed that 53.3 % (25 samples) were seriously affected by metal pollution with values above 6, and the remaining five samples were classified as having moderate and strong metal pollution in two and three samples, respectively. The value average of 12.3 computed for the whole area has indicated the area to be seriously affected by metal pollution.

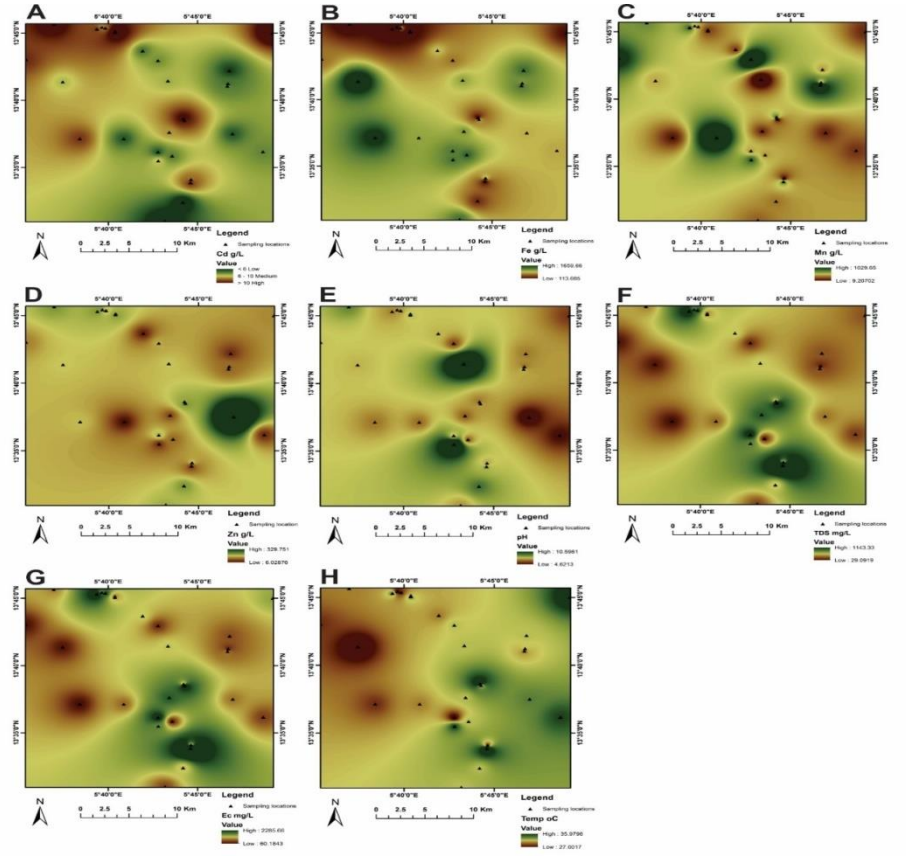

Figure 3: Spatial distribution maps of Cd (A), Fe (B), Mn (C) and Zn (D) displaying the variation in heavy metals concentrations and pH (E), TDS (F), EC (G) and temperature (H) parameters in the groundwater samples in Kaffe Study location

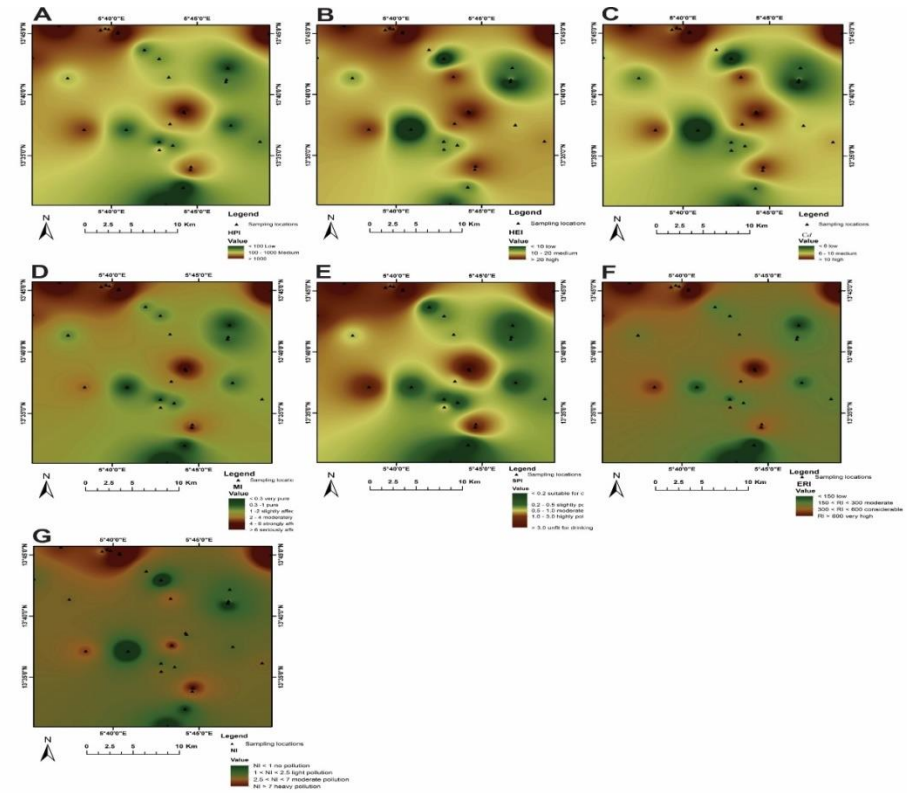

Figure 4: Spatial maps of the heavy metal pollution indices HPI (A), HEI (B), C_d (C), MI (D), SPI (E), ERI (F), and NI (G) in the study location, showing their variability..

For SPI, a more significant percentage of the sampled groundwater belongs to the class of slightly polluted groundwater, with 17 samples falling into this class which constitutes 56.6 % of the total samples analyzed in this research (Figure 4e). The remaining 13 samples (43.3%) fall in the suitable groundwater class in terms of SPI. The calculated mean value of 0.19 for this work has placed the study area under the category of suitable groundwater. All calculated ER values fall into two categories (Figure 4f) based on the given standards and classes; these are the low and moderate classes with 50 % in each category with a computed average of 148, making the area of low ecological risk potentials. Computed NI values revealed 21 samples (70 %) were moderate based on the grouping in Table 4 while 20 % of the samples used which represented six out of the total analyzed samples, and these belong to the class of heavily polluted groundwater with three samples belonging to the class of lightly polluted groundwater (Figure 4g). The study area belongs to the moderately polluted groundwater class in terms of NI based on the average value of 5.43. The spatial distributions of theseindices within the study area are displayed in Figures 4a- 4g.

Multivariate Statistical Assessments

Pearson distribution was used to correlate the different data sets and variables obtained in the study using 0.01 confidence. Of all the physicochemical parameters detected in the groundwater, only EC and TDS had a positive and strong correlation with each other (*P* 0.990). However, the Lack of any correlation between the heavy metals may indicate different sources or occurrence in the groundwater under different geochemical conditions. Strong relationships exist between the computed pollution indices and the heavy metals detected in the groundwater of the study area. Fe had a moderate correlation (*p* 0.576) with MI, while Mn shows positive and moderate correlations with HEI, Cd*,* and NI of *p* 0.699, *p* 0.700, and *p* 0.614, respectively.

For Cd, this was strongly and positively correlated to all the pollution indices determined in this study with the correlations given as HPI (*P* 0.1.000), HEI (*P* 0.800), C*d* (*P* 0.798), MI (*P* 0.981), SPI (*P* 0.993), ERI (*P* 0.999) and Ni (*P* 0.774). The correlation may arise from high Cd concentrations in the groundwater, that substantially contribute to the pollution of the groundwater resources in the area.

Although Iron (Fe) enrichment in the groundwater was also higher than the recommended limits in 29 samples, unlike Cd, it was weakly and moderately positively correlated to only SPI and MI at (*P* 0.445) and (*P* 0.576), respectively. This points to the insignificant or lesser role played by Fe in terms of groundwater pollution compared to Cd. Manganese (Mn) was positively and moderately correlated to HEI, C*d,* and NI at (p 0.699), (p 0.700), and (p 0.614), respectively. Zinc has an insignificant contribution to pollution due to the low concentration in the location.

The correlations that existed between the computed indices were all strong and positive and ranges between (*P* 0.754) and (*P* 1.000), the strongest correlation of (*P* 1.000) between HEI and Cd is an indication of their closeness in terms of methods used for their computation the same reasons is possible for strong correlations obtained between the other indices. These strong and positive correlations indicate the effectiveness of these pollution indices as thecorrect tools for evaluating heavy metals contamination or pollution of groundwater resources in the area (Table 6).

Principal Component Analysis

Four components were extracted with Eigen values (Figure 5) of one and above with a total variance of 84.97 % (Table 7). Based on Liu et al. (2015), the loading rating was classified as positive or negative, which can be strong, good, or weak (Figure 5a). The first component is loaded with all the pollution indices (HPI, HEI, C_d, MI. SPI ERI, and NI) with a contribution of 0.95, 0.93, 0.93, 0.98, 0.94, 0.96, and 0.89, respectively.

All these variables were strongly and positively loaded. Also loaded in this group were Cd and Fe with positive strong and positive weak loadings of 0.95 and 0.53, respectively. This PC compared favorably with the correlation analysis, indicating that groundwater pollution was predominantly caused by Cd, with a far lesser amount by Fe. The first component with an Eigenvalue of 7.86 contributed 52.41 % out of the total variance of 84.96 %.

The second component contributed 13.37 % of the variance with an Eigenvalue of 2.005 and was positively loaded with EC, TDS, and temperature. The EC and TDS had a strong positive loading while the temperature was weakly loaded in this group. The loading of EC and TDS of 0.81 and 0.81 respectively in this component compared favorably with the strong positive correlation obtained in the correlation analysis indicating their dependency on each other, where EC plays the role of indicator of salinization index in the groundwater. The presence of temperature 0.5, which is weakly represented in this component, can probably indicate the lesser contribution made by this parameter in the control of the dissolution of most chemical species into the groundwater.

The third PC is of no significance and was negatively and strongly loaded with Mn -0.79 of no significant impact of manganese to groundwater pollution. The PC had an Eigenvalue of 1.62 with 10.8% variance contributed. The fourth component had good loading of Zn and pH of 0.69 and -0.66, respectively, these two parameters were not involved in groundwater pollution, but they contributed 8.39 % of the total variance with an Eigenvalue of 1.26 (Figure 5b). The occurrence of pH alongside Zn in this component could suggest the role of pH in the reactions that lead to the dissolution of Zn from the rock or soil into the groundwater through absorption or adsorption processes, with the pH of the water being weakly acidic Table 6.

Cluster Analysis

The cluster analysis performed on the data set demarcates different clusters. The Dendrogram (Figure 6) shows five different clusters,with three main clusters used for the interpretation (Figure 4a). The first cluster can be compared with the First PC of the component and correlation analyses Table 7). The occurrence of these variables together indicated that they are the determining factor of the groundwater pollution status in the area and suggest a common source for the indices that most likely is Cd. The second cluster is made up of temperature, Zn, ERI, TDS, Mn, and EC. These parameters are also present in the 2nd, 3rd, and 4th components of the component analysis. The constituents of this cluster were less involved in the groundwater pollution; however, most of the components of this cluster can be considered of common origin, especially the EC and TDS. The 3rd and last cluster consisted of HPI and Fe; this indicated that Fe probably contributed to the more significant percentage of HPI due to its high concentration in the groundwater. However, the occurrence of the only HPI in the same cluster with Fe shows the latter did not make any significant contribution to groundwater pollution in the area; hence cannot be considered as a significant pollutant as far as heavy metals pollution is concern.

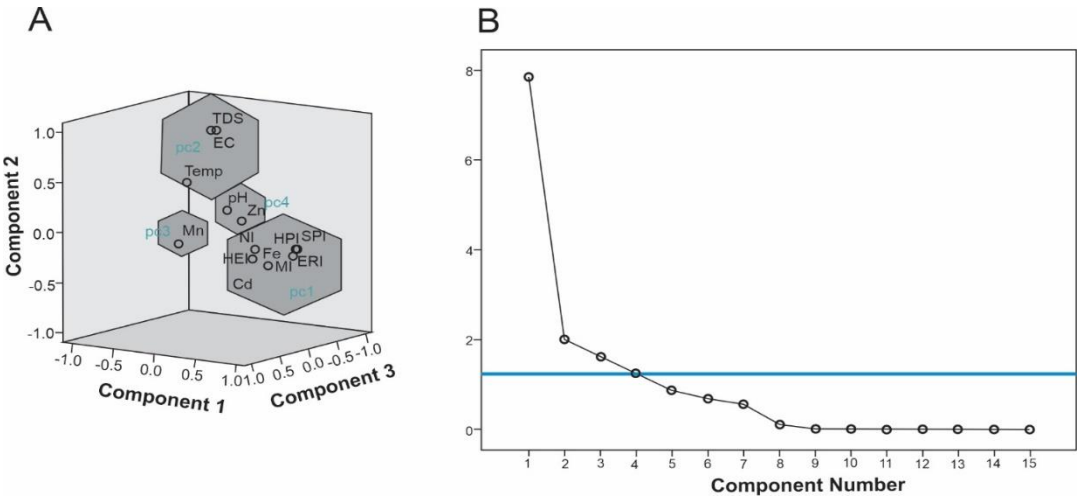

Figure 5: Rotated component and scree plot of Eigen for the parameters. A) The plot in the rotated space of the four components highlights the variables in the different components. B) Scree plot of the Eigenvalues against the components. Note the change in the curve after the fourth point as indicated by the blue line drawn across, which represents the Eigenvalues of less than one along the horizontal axis of the graph while the vertical arm of the graph represents those with Eigenvalues above one just before the red line.

Table 3: Measured elements and calculated pollution parameters in this study

Well ID	Name of Sample Locality	Cd (µg/L)	Fe (µg/L)	Mn (µg/L)	Zn (µg/L)	Temp (°C)	pH	EC (µS/cm)	TDS (mg/L)	HPI	HEI	C_d	MI	SPI	ERI	NI
1	**Gidan Alfarma**	14	1510	180	65	29	5.79	60	29	532	9.7	5.65	10.1	0.11	85.8	4.3
2	**Gidan Hashimu**	19	1140	150	70	29	6.02	500	250	758	9.1	5.1	10.4	0.15	115.5	3.5
3	**Gidan Gyado**	13	1150	90	93	30	6.11	1379	698	482	7.35	3.4	8.4	0.1	78.92	6.4
4	**Kaffe**	27	1190	9	68	31	10.6	535	265	1130	9.5	5.5	12.9	0.22	162	4.5
5	**Gada**	18	1150	340	50	29	5.98	962	471	709	10.8	6.8	10.5	0.14	111	3.8
6	**Gada II**	21	92	390	95	28	5.98	676	339	830	8.43	4.4	8.1	0.17	129.92	3.6
7	**Tudun Bulus**	26	1660	360	68	27	6.15	87	43	1085	14.35	10.4	14.9	0.21	159.6	5.3
8	**Sahil Kaura**	13	980	680	48	29	6.24	78	39	470	12.67	8.7	8.96	0.1	84.81	5.8
9	**Gidan IIIo**	24	1300	550	20	33	10.3	734	365	985	14.64	10.6	13.4	0.2	149.5	5.3
10	**Arawa**	32	1340	345	40	31	5.65	124	61	1358	14.32	10.3	15.8	0.3	195.5	5.8
11	**Kwarman Alkali (Kaddi)**	21	1220	210	30	31	5.64	875	439	850	10.4	6.4	11.5	0.2	128.1	3.9
12	**Tudun Madugu**	33	1100	240	14	30	6.16	527	264	1402	12.67	8.7	15.2	0.3	200.4	5.7
13	**Takalmawa**	31	1060	220	20	33	4.94	209	101	1309	11.9	7.9	14	0.24	188.2	5.3
14	**Tsururu**	36	1070	200	330	32	4.62	341	169	1540	12.8	8.8	16	0.3	218.07	6
15	**Gadabo**	34	1210	300	42	31	5.7	113	56	1448	13.84	9.8	15.97	0.3	207.01	5.9
16	**Mulela**	39	1320	350	20	31	5.82	245	129	1680	15.7	11.7	18.1	0.3	237.5	6.7
17	**Gadabo II**	31	1310	970	40	30	6.24	398	150	1301	20.3	16.3	16.6	0.25	195.71	8.5
18	**Tudun Bulus Junction**	30	990	990	60	31	5.49	164	81	1250	19	15.2	15.3	0.24	189.9	8.5
19	**Sabiro**	36	1190	1030	6	30	5.72	309	157	1529	21.5	17.5	18.03	0.3	226.3	9.1
20	**Gidan**	44	1035	910	40	33	6.65	186	93	1898	21.4	17.4	19.9	0.35	273.11	8.4

	Gado														
21	**Kwarman Alkali II**	36	1290	350	80	28	6.2	1100	549	1541	15	11.02	17.02	0.29	219.52	6.3
22	**Karangiya**	45	860	304	90	31	7.05	480	246	1950	15	10.9	18.5	0.36	273.1	7.4
23	**Tsitse**	47	1310	280	80	31	6	233	116	2050	16.6	12.6	20.6	0.38	284.82	7.8
24	**Dukamaje**	3	782	204	50	34	5.37	626	130	13	5.3	1.3	4	0.024	20.1	2.3
25	**Gidan Hashimu II**	13	760	520	21	36	6.56	2291	1146	469	10.34	6.3	7.9	0.1	83.2	4.5
26	**Gidan Gyado II**	6	694	610	80	36	5.71	345	173	144	9.63	5.63	5.5	0.049	42.12	4.9
27	**Gada II**	14	820	560	90	32	5.86	1297	645	516	11.2	7.2	8.5	0.12	89.62	4.9
28	**Wanlake**	5	690	490	90	30	6.83	382	192	99.9	8.23	4.22	4.96	0.04	34.92	4
29	**Borai**	4	770	220	80	30	6.28	325	163	59	5.6	1.6	4.4	0.032	26.22	2.3
30	**Fadama Borai**	3	740	250	90	32	6.44	500	249	12	5.6	1.6	3.98	0.024	20.52	2.3

Table 4: Standard and classes of computed pollution used in this study

POLLUTION INDEX	STANDARD /CLASS	NO OF SAMPLES IN EACH CLASS	STANDARD SOURCE
Heavy Metal pollution Index (HPI)	< 100 Low	4	Proposed in this study
	100 - 1000 Medium	11	
	> 1000 High	15	
Heavy evaluation Index (HEI)	< 10 Low	10	Proposed in this study
	10 – 20 Medium	17	
	>20 High	3	
Contamination Index (C_d)	< 6 Low	9	Proposed in this study
	6 - 10 Medium	9	
	> 10 High	12	
Metal Index (MI)	<0.3 Very pure		Adopted from Rezaei *et al*. (2017)
	0.3 – 1 Pure		
	1 - 2 Slightly affected		
	2 - 4 Moderately affected	2	
	4 - 6 Strongly affected	3	
	> 6 Seriously affected	25	
Synthetic pollution index (SPI)	< 0.2 Suitable for drinking	13	Adopted from Solangi *et al*. (2019)
	0.2 - 0.5 Slightly polluted water	17	
	0.5 - 1.0 Moderately polluted		
	1.0 –3.0 Highly Polluted		
	>3.0 Unfit for drinking		
Ecological risk index (ERI)	< 150 Low	15	Adopted from Taiwo *et al*. (2019), Egbueri (2020)
	150 < RI < 300 Moderate	15	
	300 ~< RI < 600 Considerable		
	RI >600 Very high		Adopted from Liu *et al*. (2015a)
Nemerow Pollution index (NI)	NI< 1 No Pollution		
	$1 \leq NI < 2.5$ Light Pollution	3	
	$2.5 \leq NI < 7$ Moderate Pollution	21	
		6	
	NI≥ 7 Heavy Pollution		

Table 5: Summary statistics of analysis compared to standards and calculated pollution indices in the area of study

PARAMETER	UNIT	MINIMUM	MAXIMUM	MEAN	STD. DEVIATION	VARIANCE	NSDWQ (2015)	WHO (2018)
Cd	µg/L	3	47	23.93	13.2	173.4	3	3
Fe	µg/L	92	1660	1057.8	306.33	93835.84	300	300
Mn	µg/L	9	1030	410.1	272.6	74286.13	200	400
Zn	µg/L	6	330	65.7	56.9	3235.33	3000	3000
Temp	°C	27	36	30.93	2.12	4.48	Ambient	32°C
PH	-	4.62	10.6	6.3	1.24	1.54	6.6-8.5	6.6-8.5
EC	Mg/L	60	2291	536.03	484.28	234525.34	1000	1000
TDS	Mg/L	29	1146	260.3	243.96	59516.47	500	500
HPI	-	12	2050	979.99	608.76	370591.24	-	-
HEI	-	5.30	21.50	12.43	4.453	19.83	-	-
C*d*	-	1.30	17.50	8.43	4.46	19.91	-	-
MI	-	3.98	20.60	12.3	5.02	25.21	-	-
SPI	-	.024	.380	.197	.109	.012	-	-
ERI	-	20.10	284.8	147.7	79.54	6326.81	-	-
NI	-	2.3	9.1	5.43	1.88	3.52	-	-

Table 6: Correlations matrix between the heavy metals in groundwater and the computed pollution indices obtained in the area

	Cd	Fe	Mn	Zn	Temp	PH	EC	TDS	HPI	HEI	Cd	MI	SPI	ERI	NI
Cd	1														
Fe	.436*	1													
Mn	.179	-.069	1												
Zn	-.005	-.175	-.262	1											
Temp	-.151	-.287	.123	-.037	1										
pH	-.003	.081	-.066	-.213	.055	1									
EC	-.284	-.261	-.116	-.046	.280	.137	1								
TDS	-.243	-.243	-.110	-.036	.244	.154	.990**	1							
HPI	1.000**	.443*	.171	-.005	-.154	-.001	-.285	-.244	1						
HEI	.800**	.444*	.699**	-.202	-.080	-.022	-.298	-.266	.797**	1					
Cd	.798**	.444*	.700**	-.201	-.081	-.024	-.299	-.267	.795**	1.000**	1				
MI	.981**	.576**	.251	-.065	-.181	.006	-.313	-.272	.981**	.864**	.863**	1			
SPI	.993**	.445*	.161	-.012	-.151	-.011	-.288	-.247	.993**	.787**	.785**	.975**	1		
ERI	.999**	.430*	.212	-.014	-.146	-.005	-.286	-.245	.999**	.818**	.817**	.983**	.992**	1	
NI	.774**	.380*	.614**	-.089	-.050	-.065	-.227	-.189	.771**	.919**	.919**	.820**	.754**	.790**	1

**. Correlation is significant at the 0.01 level (2-tailed).

Table 7: Principal component analysis for the analyzed heavy metals and computed pollution indicators for the area of study

PARAMETER	COMPONENT			
	PC1	PC2	PC3	PC4
HPI	.947	.016	.274	.074
HEI	.933	.190	-.272	-.008
C_d	.932	.189	-.275	-.008
MI	.980	.015	.192	-.017
SPI	.941	.008	.277	.072
ERI	.956	.033	.239	.082
NI	.886	.218	-.196	.109
Cd	.948	.020	.267	.079
Fe	.528	-.207	.208	-.479
Mn	.413	.370	-.786	.090
Zn	-.103	-.297	.343	.690
Temp	-.181	.495	-.171	.263
pH	-.028	.259	.186	-.659
EC	-.399	.806	.357	.056
TDS	-.360	.809	.381	.051
Eigen values	7.862	2.005	1.619	1.258
% of Variance	52.411	13.369	10.796	8.389
Cumulative	52.411	65.780	76.576	84.965

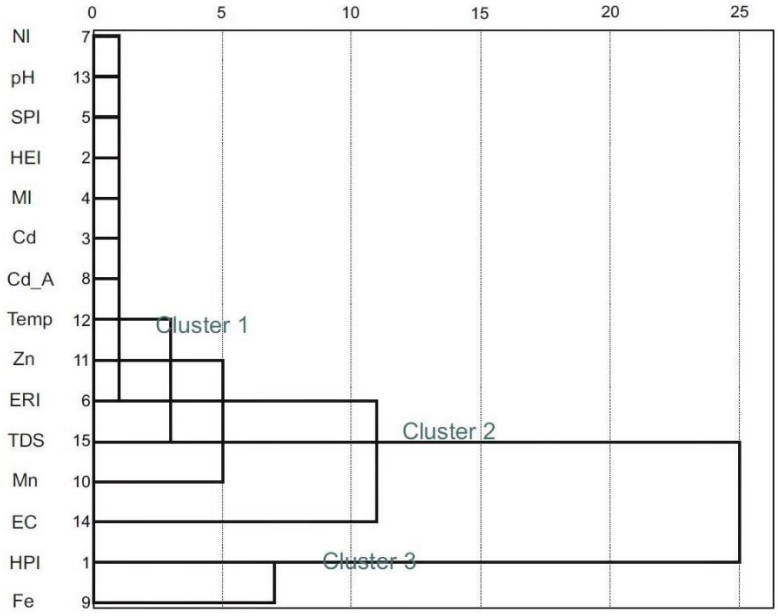

Figure 6: Dendrogram plot with three demarcated clusters using average linkage between groups.

Cadmium Geochemistry and Sources in the Groundwater

Cadmium in groundwater may originate from interlayer sites of clay minerals, from organic matter, in the soil, hydroxides, and oxides of Fe and Mn already adsorbed onto the surfaces of minerals, as well as dissolved in the groundwater (Borch *et al*., 2010). Cadmium presence in the groundwater in the study area can be linked to both natural and anthropogenic sources. Geogenic sources may include sulfides, carbonates, phosphates, and clay minerals within the sediments. These are suggested to have been mobilized from the surrounding shale,

sandstone, and limestonebased on the geology and rock types of the area.

Role of pH in Cadmium Mobilization into Groundwater

The presence of Cd, Zinc in the first cluster indicates the same properties and origin due to resemblance in their crystal-chemical nature and behaviors and the influence of pH on groundwater mobility and availability. With the average pH of groundwater being in the weakly acidic levelof 6.3, this might have facilitated Cd mobilization into the groundwater from the dissolution of its host minerals. The weathering process may have aided in the Cd leaching out of minerals and dissolving in groundwater as Cd^{2+}, forming complexes with Cl^{-}, (OH^{-}), (SO_4^{2-}), (HCO_3^{-}), and (CO_3^{2-}).

However, anthropogenic Cd input into the groundwater may have originated from phosphate fertilizers, organic manure, and pesticides used in farms and irrigated parts of the study area. Additional contributing sources may include atmospheric deposition or acidification linked to the denitrification process of NPK fertilizers used on farmlands, fossil fuel combustion, bush burning, and defecations. Grant (2011) pointed out that in addition to Cd input, phosphate fertilizers application also decreases Cd sorption because of the competition of other components like NH_4 or Zn, which can replace Cd from binding sites.

Cadmium Geochemistry and Mobility in Groundwater

Weathering process leads to leaching out and dissolution in groundwater Cd^{2+} in the form of a complex with any one of the following ligands (SO_4^{2-}), (HCO_3^{-}), ($CO3^{2-}$) Cl^{-}, and (OH^{-}). At a high pH value of 7 and above, the tendencies of formation of complexes are very high hence making the groundwater pH the main controlling factor that determine the availability of binding site on the aquifer surface (Wang *et al*., 2010). Additionally, similarities in ionic radius with other metals with divalent cations (Ca Fe and Zn), Cd can replace them in complexes in groundwater (Earon *et al*., 2012). Thus, coprecipitation with dissolved Fe and Mn is essential for the environmental fate of Cd. The mobility and concentration of Cd in the groundwater can be related to the pH of sampled water. The pH range of 4.6 – 10.6 was recorded in this study, with only 3 out of the values recorded as alkaline (7.05 -10.6). The remaining 27 samples had pH values of between 4.6 and 6.8, indicating acidic conditions. Comparing the pH values and the Cd concentrations range obtained for the groundwater in the area of 3 – 47 µg/L, we suggest acidic pH conditions of the water may have been responsible for Cd dissolution from its host minerals in the rocks.

This finding agrees with those of other authors on the influence of pH on the mobility of Cd and other heavy metals in groundwater (Gong *et al*., 1977; Bruemmer *et al*., 1986; Loganathan *et al*., 2012; Naseem *et al*., 2012).

Cadmium Geochemistry

Considering the obtained cadmium concentrations of all the groundwater samples used in this research as given in Table 3, only the sample collected from Fadama Borai had a Cd concentration that is not above the WHO and NSDWQ limits of 3 µg/L. The remaining samples contain a Cd concentration between 4 to 47µg/L. Smolders and Mertens (2013) suggested that Cd tends to exist as a divalent Cd^{2+} cation in solution. However, Cadmium chooses to remain in solution at a pH of below 6.5 under oxygenated conditions (Merkel and Sperling, 1998). The pH of the solution has the leading influences on the mobility and availability of Cd. Other factors that control Cd concentration in the solution includethe solubility of organic matter, the surface charge of oxy-hydroxides, metal hydrolysis, organic matter, ion-pairformation, and clay edges (Kubeir *et al*., 2019); this is the most probable cause for the high concentration of Cd in the study area. Another possible factor responsible for the high concentration of cadmium in water could be due to the lesser ability to form complexes with other compounds as pointed by Eggleton and Thomas, (2004) and Caetano *et al* (2003), Cd is mostly bound to the less stable exchangeable carbonate and hydrous oxide in complexes. The bound makes it easier for cadmium to get mobilized into solution than other heavy metals like Pb and Cu. Cd is comparatively more mobile than other heavy metals such as Ni, Pb, and Cu due to the difference in the mineral solubilities and sorption behavior.However, complex formation by Cd and other heavy metals is controlled by factors like the ionic strength effects, the presence of ligands, and the presence of competing cations such as Ca (Beisecker *et al*., 2012).

Similarly, Carrillo-Gonzalez *et al* (2006) suggest that Cd concentrations in groundwater are often controlled by sorption and coprecipitation. A comparison betweenCd and Zn showed that these metals have similar geochemical behavior. Thornton (1986) and Beisecker *et al* (2012) confirmed that although the limiting pH of Cd mobility is 6.5, this is higher compared to that of Zn, which is between 5.5 and 6.0, while other heavy metals have the following pH mobility ranges (Ni 5.5; Co 5.5; Cu 4.5; Cr 4.0 to 4.5; Pb < 4). The above geochemical processes and reactions of sorption, complexing, dissolution, and mobilization occurring between the groundwater, the rock matrix, and minerals as well as organic materials and other metallic and nonmetallic components of soil and rocks are the important factors processes that led to the mobilization and concentration of cadmium in groundwater.

CONCLUSION

The groundwater resources from the Kaffe community and environs were assessed to determine the pollution and contamination status regarding Cd and other heavy metals. Results show Cd and Fe concentrations in the groundwater exceed the recommended limits of WHO and NSDWQ in 96.7 % of analyzed samples with Cd dominance over the other metals given in the order Cd

>Fe >Mn >Zn. Heavy metals pollution assessment indicates moderate pollution regarding HPI, HEI, C*d*, and NI. However, the mean values of 12.3, 0.19, and 148 obtained for MI, SPI, and ERI reveal variable suitability. A strong positive correlation between Cd and pollution indices are indicative of the former's central role of groundwater pollutant in the Kaffe region. The Cd is suggested to have been mobilized into the groundwater, aided by the pH and Zn concentrations. Two possible originshave been identifiedas theprimary sources of Cd concentration and mobility in groundwater. 1) weathering from surrounding sedimentary rocks through processes that include sorption, adsorption, and coprecipitation from rock matrix and mineral surfaces. 2) anthropogenic sources arising from agricultural activities and waste disposal in the area.

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