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Trace Metals in Groundwater of Kumba and Environs in Cameroon

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Abstract

Kumba and environs situate between longitudes 9.24E - 9.5E and latitudes 4.44N - 4.7N, is the economic capital of the Southwest Region-Cameroon. It is located along the Cameroon Line at northwestern edge of the Douala Basin. The inhabitants depend mostly on groundwater through springs, handdug wells and boreholes. In this area like in most of Cameroon and Africa, water from groundwater sources (springs, wells and boreholes) is not treated. Often, it is given minimal or cosmetic periodic treatment if at all. Although the concentrations of trace metals in groundwater affects its safety and acceptability, testing for trace metals is less common and typically occurs mostly when a specific risk has been identified. This could be attributed to the high cost of analysis and lack of technological know-how. In addition to this, testing and monitoring of groundwater is not carried out most of the time and whenever it is done, only major cations and anions are analyzed. Due to the absence of treatment and testing of groundwater before drinking in Kumba and environs, there is a need to evaluate the trace metal content. The study had 21 groundwater samples analyzed using Inductively Coupled Plasma Mass Spectroscopy. Field measurement of physicochemical parameters was determined. R-mode statistical analysis; Pearson's Correlation Analysis (PCA) together with Hierarchical Cluster Analysis (HCA) between the trace metals and the physico-chemical parameters was carried out. Ten indices were determined: Four trace metal hazard indices: the average daily dose ADD, carcinogenic risks CR and the non-carcinogenic risk hazard quotient HQ which yields the hazard indices HI, and six trace metal pollution indices: Degree of contamination (DC), Enrichment factor (EF), Ecological risk index (Er), Potential ecological risk index (RI), Pollution load index (PLI) and Geo-accumulation index (Igeo). The general trend of mean trace metal concentration in the groundwater is in the order of: Mn > Fe > Ba > Sr > Zn > Ni > Cu > Co > Pb > Li > Cr > V > As > Cd. HCA distinguishes two clusters based on spatial similarities and dissimilarities. Cluster one; (01) element Ba; soluble; Cluster two (13) non soluble elements divided into three classes; class one (06) As, Cd, V, Li, Pb, and Cr; less enriched. Class two (03) Co, Cu, Ni and Zn; enriched; Class two (04) Zn, Sr, Fe and Mn; more enriched. Values of pollution indices range as follows; DC (−13.53 to 12.1), EF (1.15 - 874.13), Er (−29.68 to −0.97), RI (−61.06 to −43.03), PLI (−0.01 - 0.05), Igeo (7E−08 - 287). Almost all are below the acceptable guideline values. While values of groundwater hazard indices range as follows; ADD (1.01E−06 - 0.05), CR (8.5E−06 - 0.018), HQ (3.3E−04 - 1.59) and HI (0.07 - 1.59). The groundwater hazard indices: ADD and CR are less than 1 in the categories of insignificant pollution health hazard, are below the acceptable guideline values whereas HQ and HI are above 1, likely to pose health hazards. Igeo values indicate groundwater is Unpolluted to moderately polluted by Pb, V, Cr, Co, As, Cd, Pb; while it is Extremely polluted by Mn, Fe, Ni, Cu, Sr, Zn, Ba. The enrichment factors show that the sources of the trace metals are from geogenic and anthropogenic processes. Ba and Co are enriched although they fall below the hazard risk values; this shows they have pollution potential that could be attributed to weathering and agricultural wastes. The severity of metal toxicity is governed by several factors, such as dose, nutrition, age, and even life style. Therefore, these low trends might not guarantee the complete absence of human health risks. Generally, from risk assessment on trace metals using risk indices in the analyzed groundwater samples might not cause any health risk. However, due to an increasing level of environmental pollution that might be imposed by increasing human activity in this area, groundwater sources might become a potential sink of contaminants; this is significant reason that makes constant monitoring, implementation and treatment of groundwater for drinking purposes necessary.

Subject Areas

Environmental Sciences

Keywords

Health-Hazard-Indices, Pollution Risks-Indices Trace-Metal, HCA, PCA, Kumba, Cameroon

1. Introduction

Kumba and environs situates between longitudes 9.24E - 9.5E and latitudes 4.44N - 4.7N **Figure 1**; is the administrative headquarters of Meme Division and economic capital of Southwest Region of Cameroon. It is at the center of one of the largest cocoa cash crop producing areas in the country.

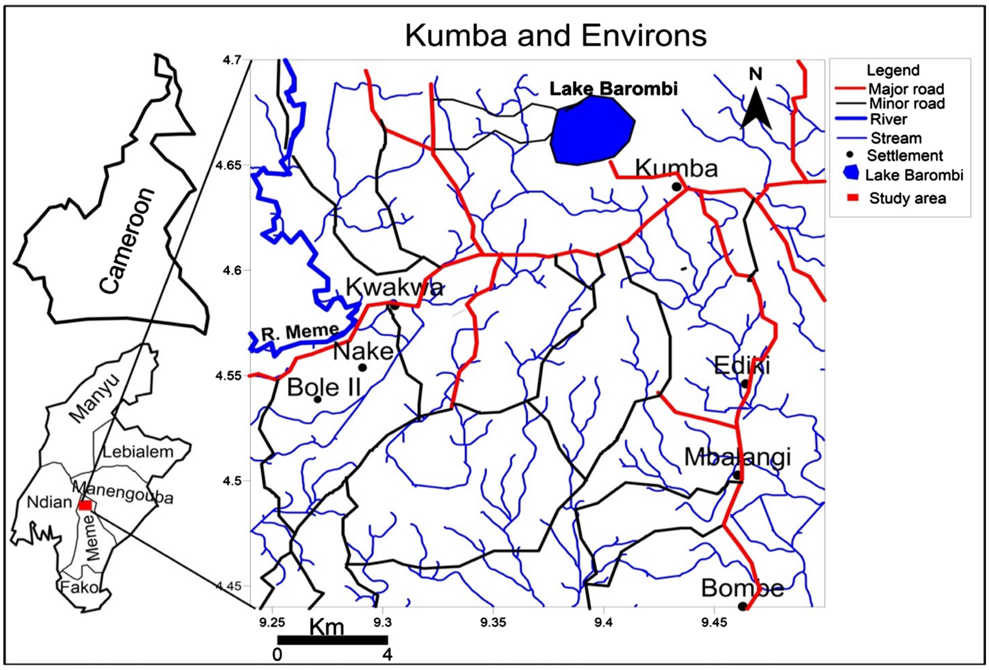

Figure 1. Location map for *measurements and sample collection in Kumba and environs.*

This area is an agro-industrial zone of cocoa production which is exported and dependent on groundwater. The assessment of trace metal quality of springs, dug wells and borehole water exploited for consumption by more than 90% of inhabitants of this area is sparse. Therefore a series of health risks and pollution risks associated with elevated trace metals concentrations in groundwater may arise if the trace metal concentrations of groundwater in this area is high [1].

Trace metals are chemical components found in low concentrations, in mass fractions of ppm or less, in water, organisms and soil [2]. Some trace metals are essential as micronutrients Cu, Fe, Mn, Ni and Zn for life processes in plants and microorganisms, while others Cd, Cr and Pb have no known physiological activity, but are proven detrimental beyond a certain limit which is very much narrow for some elements like Cd 0.01 mg/L, Pb 0.10 mg/L and Cu 0.050 mg/L [3]. These toxic metals, unlike some organic substances, are not metabolically degradable and have the tendency to bio-accumulate in tissues of living organisms over time which can cause death or serious health threats [2]. The presence of trace metal species in groundwater can be of geogenic or anthropogenic origin. Natural or geogenic contamination occurs when the weathering of minerals in rocks results in the entry of heavy metals into the environments and water bodies are retained in the groundwater/soil and do not readily leach out; accumulate through geological processes, enter the food chain through ingestion and ultimately pose a threat to humans, animals and plants. By ion exchange, precipitation, dissolution or mixing, trace metal ions contained in the rocks are introduced into the water. These metals exist in water as colloidal, particulate and dissolved species. Anthropogenic contamination occurs through the development of industrial agriculture, mining, smelting and other industrial activities.

Metallic elements have a significant role in increasing the degradation of water quality through human activities; industrial-household wastes, thermal power plants, mining, exhaust emissions, application of fertilizers, pesticides and insecticides. Trace metals pose a severe threat to human and environmental health since these elements are toxic at low concentrations and pollution caused by these heavy metals is long-term and irreversible; cumulative. Trace metals are increasingly being found in groundwater sources. The exposure to trace metal contamination and associated health risk levels of the population in Akwa-Mundemba has not been investigated hence; the quantification of trace metals for suitability of the groundwater resources for drinking, domestic and agro-industrial uses is of public health and scientific concern. It has been recognized for many years that the concentrations of metals found in coastal areas, whether they are in the dissolved or particulate phase may be derived from a variety of anthropogenic and natural sources. In most circumstances, the major part of the anthropogenic metal load in the marine sediments and organisms has a terrestrial source from mining and intensive aquaculture and municipal wastewaters, untreated effluents, harbor activities, urban and agricultural runoff along major rivers, estuaries and bays. These elements are: Antimony, Arsenic, Boron Barium, Bromine, Cadmium, Cesium, Chloride, Cobalt, Copper, Fluoride Iodine, Iron, Lead, Lithium, Manganese, Mercury, Molybdenum, Nickel, Phosphorus, Rubidium, Selenium, Strontium, Uranium, Vanadium and Zinc.

The study aims to improved knowledge on the occurrence of trace metals in groundwater in Kumba and environs, which will:

- Provide better information on concentration ranges in groundwater.
- Act as basis for future regulations on trace metals in drinking water from this area.
- Provide estimates of the contribution of groundwater to overall trace metal intake.
- Provide baseline on trace metals in the groundwater if challenges arise in the future.
- Estimate the health hazard and pollution indices of trace metals in groundwater.

1.1. Climate

Kumba generally has a hot and humid equatorial climate with two seasons: a short dry season of about 4 months (December to March) and a long rainy season (April to November). Annual rainfall ranges from 2298 mm to 3400 mm. The average annual temperature is approximately 27˚C.

1.2. Vegetation

Kumba is located in the tropical rainforest with vegetation that varies from savannah to forest (around Lake Barombi Mbo). The evergreen and semi-deciduous forests contain economically important tree species (iroko, mahogany, obeche, ebony, padouk, tiama, framire, sapelline, makore and bobinga, etc.). The herbaceous layer is dominated by Pennisetum, purpureum and Imperata cylindrica with a ligneous cover that is heavily affected by human activity. The river valleys are covered with Indian bamboo (Bambousa species) whose stems are used for handicraft activities. Deforestation is the main cause of environmental degradation in Kumba. It arises from human activities, especially inappropriate farming practices (shifting cultivation), over grazing, bushfires, poaching and illegal logging.

1.3. Geology

Kumba is located in the Kumba Plain, a graben intercalated between the strato-volcanoes of Mt Cameroon and Mts Rumpi, at the northwestern edge of the Douala Basin as in Figure 2. The Cameroon Line (CL) is an alignment of Tertiary-to-Recent alkaline volcanoes, plutons and grabens extending over more than 1600 km stretching from the Atlantic oceanic island of Annobon through the Gulf of Guinea and within the African continent. The Douala basin probably formed from a Precambrian cratonisation, granitisation and sedimentation phase followed by the Pan-African orogenesis, the Afro-Brazilian depression (the site of the future Cameroon Atlantic basin) with epi-continental sedimentation which may have begun during the lower Cretaceous, discordant Cretaceous to Pliocene sediments on the Precambrian Pan-African basement and covered in

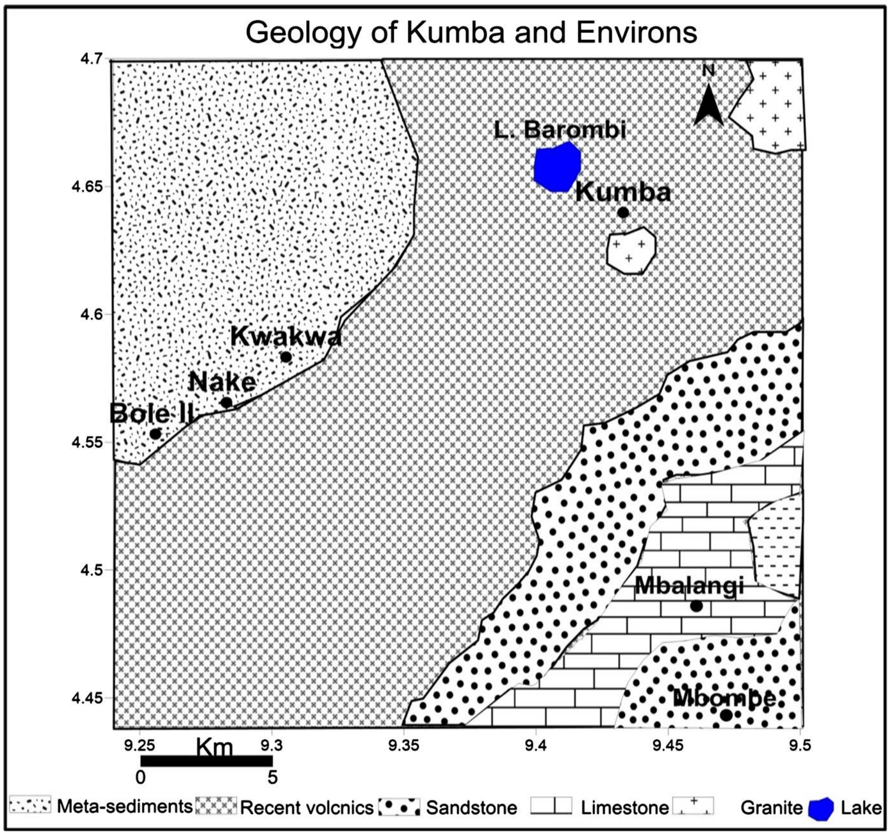

Figure 2. Geologic map of study area made up of four rock types; metasediments, recent volcanics, sandstones, limestone and granites.

some areas by Miocene sedimentation and volcanism. The geology of the Kumba Plain (Kumba Volcanic Field) is controlled by three main volcanic activities (which probably occurred between the Eocene and 1 Ma ago). These include: old basaltic lavas covering the entire plain; cinder cones and phreatomagmatic units; and short vesicular basaltic lava flow.

There are 4 maars in the Kumba Plain. These include: the Barombi Mbo, Barombi Koto, Mbwadong and Dissoni Maars, with the first two occupied by Lakes Barombi Mbo and Lake Barombi Koto. Based on the composite fragments contained in the Barombi Mbo Maar (BMM) pyroclastic deposits, it is likely that the maar cuts through a geological succession composed by granite gneissic formation, sandstones, and basaltic lava flows; the same formations that make up the Kumba volcanic field.

Volcanic formations of the plain have been emplaced over Pan African metamorphic formations intruded by granitoids and locally covered by Cretaceous continental sandstones. They commonly enclose mantle peridotite xenoliths [4].

1.4. Hydrogeology

Weathered basement (regolith), fractured-gneiss, basalts, pyroclastics and recent alluvium are the aquiferous formations in the area. Saturated hydraulic conductivities of the aquiferous formations range from 2.88E−08 to 1.60E−06 m/d [5], groundwater velocities from 1.96E+01 to 6.34E+02 m/d [4], first estimates of well yields from 4.6E−01 to 2.28E+01 m/d and the hydraulic conductivities of the vadose zone from 7.96E+02 to 3.27E+04 m/d. and stream discharges 1.79E+05 to 9.13E+05 m^3/d [6].

Prior to sampling, the pre-cleaned sample bottles were rinsed with the sample water. The well water was withdrawn with the use of a 50 ml syringe, and then filtered through the 0.2 μm mixed cellulose ester filter into 50 ml high-density polyethylene HDPE containers. The sample was preserved by acidifying to pH < 2 by adding nitric acid and sealed using a permanent tape. The samples were labelled and put into the sample bottle collection bag. The filtered groundwater samples were later shipped to the Activation laboratory in Canada for trace metal analysis by Inductive Coupled Plasma Mass Spectrometer ICP-MS.

2. Materials and Methods

2.1. Sample Collection, Pre-Treatment and Chemical Analysis

Twenty one samples were collected from 21 pre-selected wells, boreholes and springs. Site selection was based on spatial distribution of the wells, boreholes, springs and population. At each site, groundwater temperature, electrical conductivity, total dissolve solids and pH value were measured in situ, using portable field pH, EC and TDS meters as shown in Table 1.

2.2. Hazard Identification

It involves the identification of the chemical of concern and documenting its toxic effects on human beings after field mapping. It also involves the characterization of potential contaminants and their relative mobilities [7] as shown in Table 2.

2.3. Exposure Assessment

This is the process of measuring or estimating the intensity, frequency and

Table 1. Field Equipment, Softwares, their specifications and functions used in the study.

Equipment/Softwares	Specifications	Functions
Bike	Commercial Bikes (Bensikin)	To transport fieldworkers to wells
GPS	GARMIN GPSMAP 60 csx	To measure longitude, latitude and elevation of wells
EC Meter	Hanna Hi 98304/Hi98303	To measure Electrical Conductivity of water.
pH Meter	Hanna Hi 98127/Hi98107	To measure pH of water.
Measuring Tape	Weighted Measuring Tape	Measurement of well diameter and depth.
Digital Thermometer	Extech 39240 (−50˚C To 200˚C)	To measure water temperature
Total Dissolved Solid	Hanna HI 96301	To measure Total dissolved solids
Water sampler	Gallenkampf 500 ml	To collect water sample from well
Syringe	50 Ml, 100 Ml Polystyrene	Acidification and filtration of sample
Nitric acid	98% Pure Nitric Acid	Sample preservation by acidifying to pH < 2
Filter	Cellulose Ester Filter 0.2 µm	Filtration of sample
Sample bottles	Polyethylene (HDPE) 50 ml	To hold sample for onward transmission to laboratory
Sealing Tape	Permanent Tape and marker	Sealing of sample bottle and labeling for the laboratory
IBM SPSS Statistics	Version 24.0	Statistical analysis for PCA
Global Mapper	Version 11	GIS Geolocation of wells
Surfer Golden Software	Version 12	GIS plotting contours for spatial distribution

Table 2. Trace metals and their effects [2].

Component	Toxicity effects
Zn	Zinc suppresses copper and iron intake causing peripheral neuropathy.
Co	Active in vitamin B12 and in chemical reactions. Excess causes hearth failures.
Cu	Excess leads to acute gastrointestinal problems
Cr	Excess may result in renal failures. Excess of Cr^{+6} is carcinogenic.
Mn	Manganese toxicity result in neurological disorder; manganism, with symptoms of tremors
Cd	Cadmium compounds are known human carcinogens.
V	Vanadium causes albumin in urine
Ni	Nickel is carcinogenic and causes neurological deficits
As	Arsenic causes cancer of the skin, lungs, liver and bladder.
Sb	Antimony causes gastrointestinal problems, kidney damage or liver damage
Al	Aluminium causes neurotoxicity.
Pb	Lead is a carcinogen affecting every organ and system in the body.

duration of human exposures to an environmental agent [7]. The main exposure pathway taken into consideration in this study was intake of the metals through water consumption. The daily environmental exposures to metals were assessed for carcinogenic and non-carcinogenic elements.

The intake of metals through ingestion of groundwater were calculated using Equation (1) [8].

$$ADD = \frac{C \cdot IR \cdot ED \cdot EF}{BW \cdot AT \cdot 360} \quad (1)$$

where:

ADDs is Exposure duration (mg/kg-day)—The Average Daily Dose (ADD) of the contaminant through water pathway indicates the quantity of chemical substance ingested per kilogram of body weight per day.

C is Concentration of contaminant in the environmental media (e.g., μg/L, mg/L).

IR is Ingestion rate per unit time (e.g., mg/day or L/day).

EF is Exposure frequency (day/year).

ED is Exposure duration (years).

BW is Body weight of receptor (kg).

AT is Averaging time = life expectancy (years) 365 is the conversion factor from years to days.

For non-carcinogenic effects, AT = ED in days; carcinogenic effect, AT = 70 years or 25,550 days [8].

2.4. Dose-Response/Toxicity Assessment

This is the quantitative relationship that indicates the contaminants degree of toxicity to exposed species. It also involves the identification of the toxicity criteria used to evaluate human health risk associated with the chemical of concern in the study area. The amount of chemical that can affected human health is estimated. The Reference Dose RfD is used for non-carcinogen risk.

2.5. Risk Characterization

This is the final phase of the risk assessment process. In this phase, cumulative exposure and dose-response assessments are integrated to yield probabilities of effects occurring in human beings under specific exposure conditions and time scales. Also incorporated is information from hazard identification, exposure assessment, toxicity assessment and risk estimation to evaluate the potential risk to residents.

2.6. Carcinogenic Risk Assessment

Carcinogenic risks was determined by calculating the potential of an individual to develop cancer as a result of cumulative exposure to each potential carcinogen over a lifetime. For carcinogen, identified by a weight-of-evidence classification of the chemical [9].

The estimated daily dose and the cancer slope factor are multiplied together to find the lifetime cancer risk posed by the chemical. Cancer slope factors are estimates of carcinogenic potency and were used to relate estimated daily dose of the trace metal over a lifetime exposure to the lifetime probability of excess tumors Equation (2) [9] [10] [11].

$$CR = ADD \cdot SF \tag{2}$$

CR is the excess probability of developing cancer over a lifetime as a result of exposure to a contaminant or carcinogenic risk. It is unit less; SF is the slope factor of the contaminant $[mg/kg/d]^{-1}$.

2.7. Non Carcinogenic Risk Assesment

Non-carcinogenic hazards are characterized by the hazard quotient (HQ). HQ is a unitless number that is expressed as the probability of an individual suffering an adverse effect. To estimate noncarcinogenic risk, the hazard quotient (HQ) was calculated using Equation (3) [12].

$$HQ = \frac{ADD}{RfD}, \tag{3}$$

RfD is the reference dose mg/kg/d. It represents a toxicity index of a daily exposure to the population in comparison to a safe level of exposure orally over a lifetime [13].

2.8. Harzard Index (HI)

It is the toxic risks due to all the potentially hazardous substances present in the same media simultaneously [14]. Since more than one toxicant is evaluated, the interactions of all the toxicants were considered and assumed to be cumulative. Thus, the HI was calculated by summing all the HQ for all toxicants, Equation (4) [12].

$$HI = \sum_{i=1}^{n} HQ_i \tag{4}$$

2.9. Pollution Evaluation Indices

Generally, pollution indices are estimated for a specific use of the water under consideration. The trace metal degree of contamination (DC), enrichment factor (EF), ecological risk index (Er), potential ecological risk index (RI), pollution load index (PLI) and geo-accumulation index (Igeo) were used to evaluate the pollution potential of the study area (**Table 3**).

3. Results and Discussion

3.1. Physicochemical Parameters

The physicochemical parameters groundwater in the study area: temperature, pH, EC and TDS were evaluated as shown in **Table 4**.

3.2. Water Level Fluctuations

Depth-to static water level (m) of groundwater ranged from: 0.2 - 6.2 m as in

Table 3. Formulae for calculation of pollution indices.

Trace element pollution indices	Formulae	Reference
Degree of Contamination	$\mathrm{DC} = \sum_{i=1}^{n} C_f^i$	(Edet and Offiong, 2002) [15]
Enrichment factor	$\mathrm{ER} = \frac{(\mathrm{Ci/Cie})\,\mathrm{sample}}{(\mathrm{Ci/Cie})\,\mathrm{background}}$	(Zhang *et al.*, 2007) [16]
Ecological risk factor	$\mathrm{Eir} = \mathrm{Tri} \times \mathrm{Cfi}$	Håkanson, (1980) [17]
Ecological risk index	$\mathrm{RIi} = \sum_{i=1}^{n} E_r^i$	Håkanson (1980) [17]
pollution load index	$\mathrm{PLI} = \sqrt[n]{C_{f1} \times C_{f2} \times \cdots \times C_{fn}}$	(Harikumar *et al.*, 2009) [18]
Geo-accumulation index	$\mathrm{Igeo} = \log 2\left[\mathrm{Ci}/(1.5\mathrm{Cri})\right]$	(Ji *et al.*, 2008) [19]

Table 4. Field determined physicochemical parameters; electrical conductivity (EC), pH, total dissolved solids (TDS) and temperature of groundwater in study area.

Parameter	Min	Max	Mean
T (˚C)	26.7	29.1	27.7
PH	2.3	6.4	5.1
EC (mS/cm)	1.8	50.1	17.7
TDS (mg/L)	1.2	33.6	11.9

Figure 3. Areas with low depths to static water levels such as; Kumba, Ediki, Bombe and Kwakwa are susceptible to pollution if the wells are not appropriately constructed and protected.

3.3. Groundwater Flow Direction

Groundwater flows towards the Southwestern and Northwestern parts of the study area which could probably be a recharge zone as in Figure 4.

3.4 Temperature

Temperature values of groundwater ranged from: 26.7˚C - 29.1˚C as seen in Figure 5. The temperature variation is similar in the different areas, suggesting a single aquifer since groundwater in the same aquifers have similar parameter values and temperature is one of them.

3.5. pH

The pH value of most of the groundwater samples in the study area ranged from 2.3 - 6.4 as in Figure 6. The value of pH of a water sample is recognized as an index of classifying groundwater as acidic < 5.5, slightly acidic 5.5 - 6.5, neutral 6.5 - 7.5, slightly alkaline 7.5 - 8, moderately alkaline 8 - 9 and alkaline > 9. This clearly shows that the groundwater in the study area is acidic to slightly acidic.

3.6. Electrical Conductivity

The EC ranged from 1.8 - 50.1 mS/m as in Figure 7. The low electrical conductivity

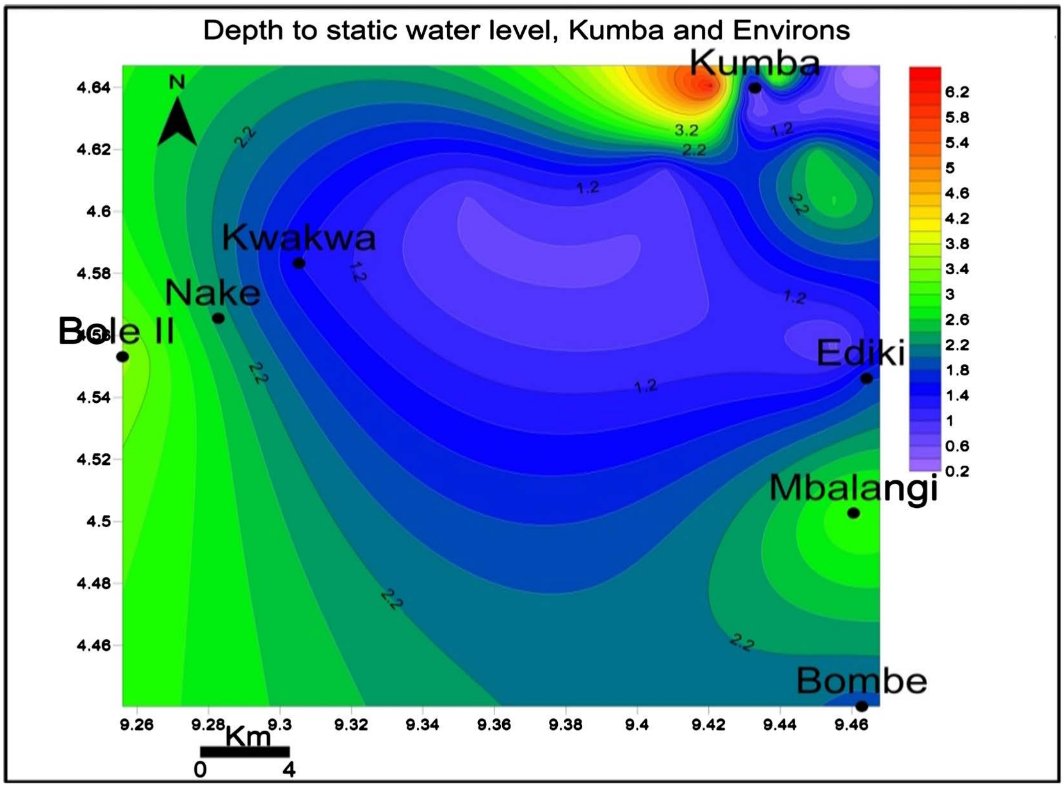

Figure 3. Depth to static water level; high values are at Mbalangi, Bole II and Nake whereas low values are at Kumba, Ediki, Bombe and Kwakwa.

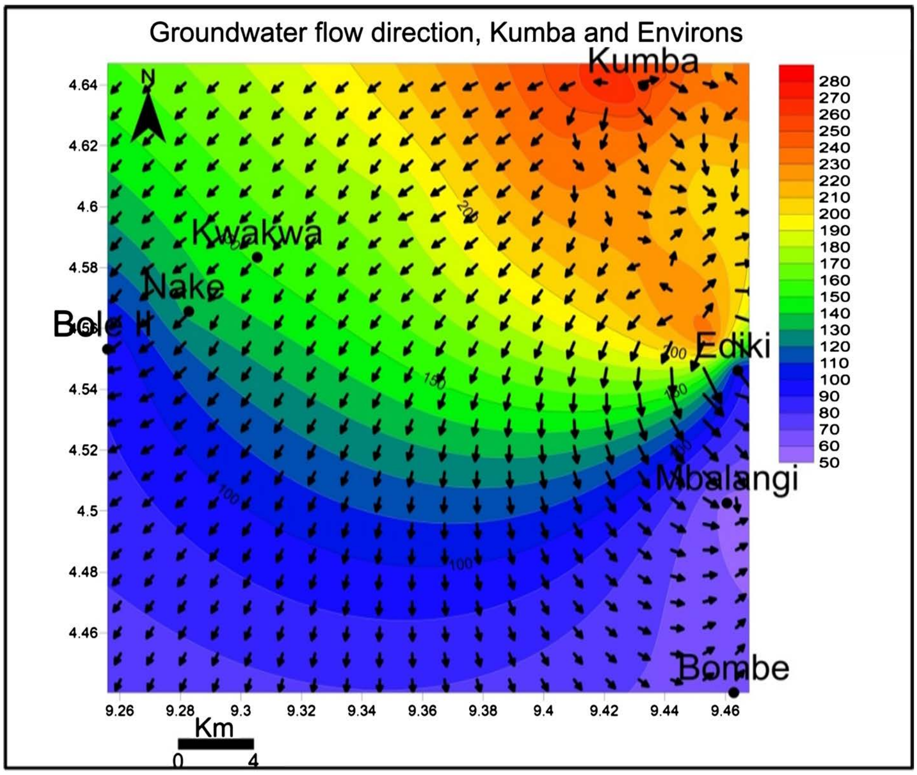

Figure 4. Groundwater flow direction in study area indicating that water flows towards the Southwestern and Northeastern parts of the study area.

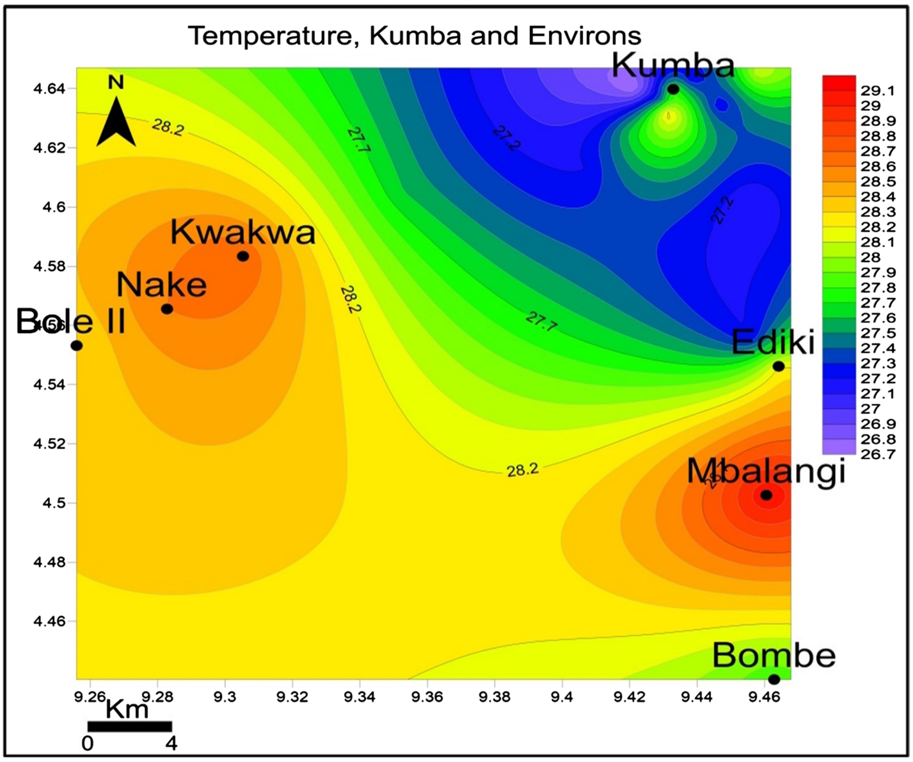

Figure 5. Spatial variation of groundwater temperatures; Temperatures are generally higher at Mbalangi, Ediki, Bole II, Kwakwa and Bombe while low values are at Kumba.

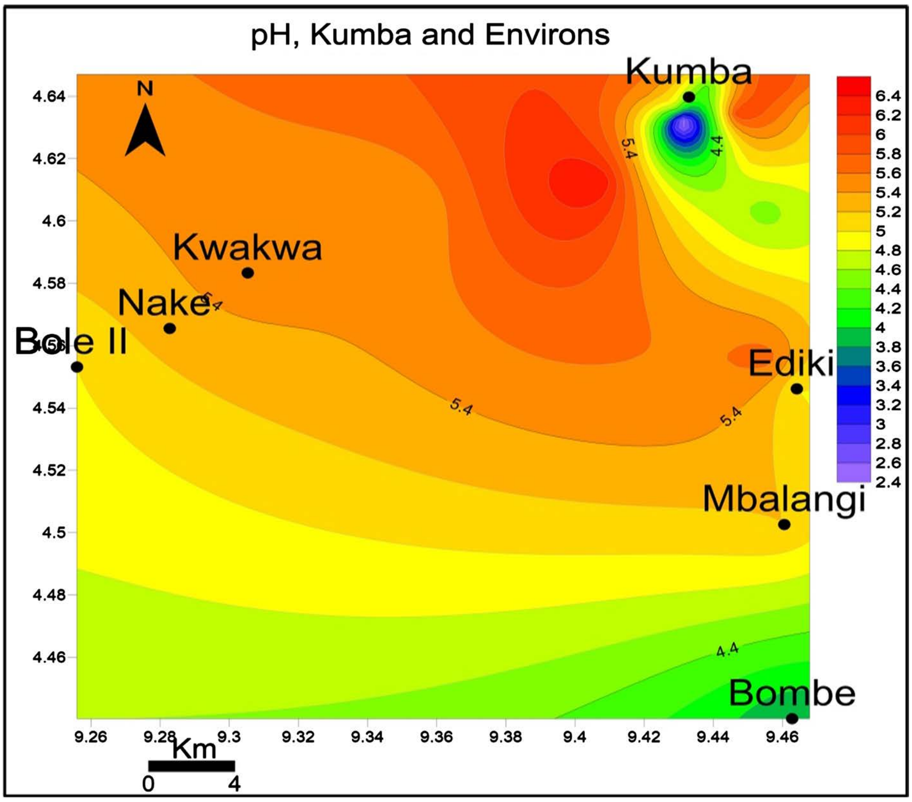

Figure 6. Spatial variation of pH; High pH values are at Mbalangi, Bole II, Nake, Kwakwa and Ediki while low values are at Kumba and Bombe.

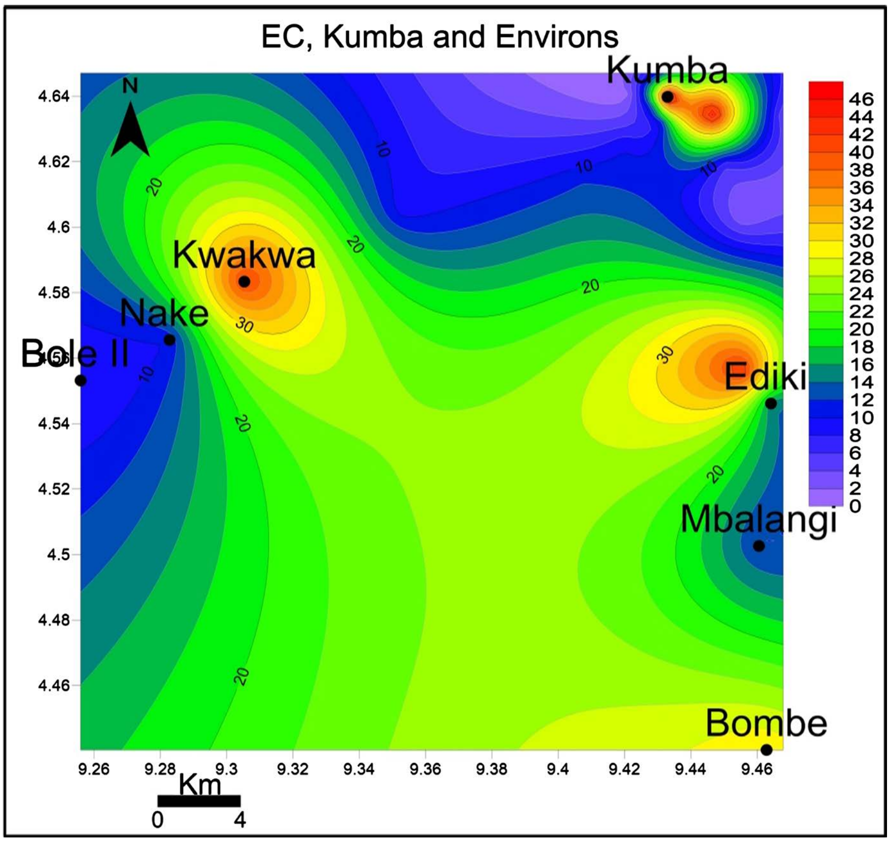

Figure 7. Spatial variation of Electrical Conductivities (mS/m); EC is at maximum at Kumba, Kwakwa, Ediki and Bombe while minimum values are at Nake, Bole II, and Mbalangi.

is due to less solute concentration in groundwater.

3.7. Total Dissolved Solids

The total dissolved solids ranged from 1.2 - 33.6 mg/L as in Figure 8. These TDS values are < 500 mg/L thus indicating that the water is fresh.

3.8. Trace Metal Concentration

The results for twenty one samples of trace metal analysis ICP-MS are presented in Table 5. The concentrations of fourteen trace metals; Mn, Fe, Ba, Sr, Zn, Ni, Cu, Co, Pb, Li, Cr, V, As, and Cd were evaluated since they were of significance. All concentrations of these trace metals are below the [20] allowable limits Mn and Ba which had concentrations above permissible limits. However, the cumulative effects of long term consumption of these trace metals in the groundwater necessitated a health risk assessment.

Average concentrations of these trace metals were in the decreasing order as follows in μg/L: Mn (193.11), Fe (151.71), Ba (142.32), Sr (65.78), Zn (60.29), Ni (14.15), Cu (10.12), Co (7.47), Pb (2.31), Li (1.62), Cr (1.53), V (0.72), As (0.21) and Cd (0.16). The trace metal with the highest concentration is Mn with a maximum value of 687.20 μg/L detected at Bombe.

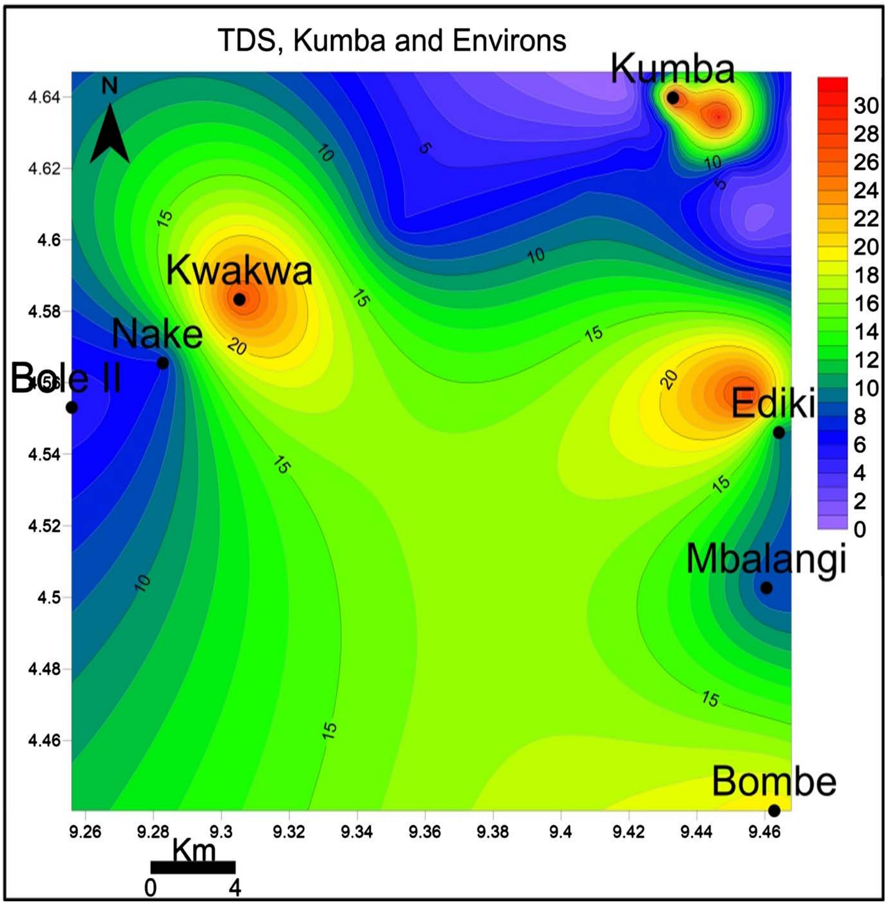

Figure 8. Spatial variation of total dissolved solids mg/L; TDS is maximum at Kumba, Kwakwa, Ediki and Bombe while minimum values are at Nake, Bole II, and Mbalangi.

3.9. Pearson's Correlation Analysis PCA between Trace Metals and Physico-Chemical Parameters

Correlation between trace metals in groundwater within the study area was carried out using Pearson's correlation analysis (PCA) as shown in Table 6 to establish the relationships that exist between the variables; trace metals and the physico-chemical parameters as in Table 2. r values > 0.5 or < −0.5 are significant, 0.72 strong (moderate) and 0.80 Very strong correlation.

In Table 6, a very strong positive correlation exists between the following; Pb and Cu (r = 0.82), Cd and Zn (r = 0.86), EC and As (r = 0.98), TDS and As (r = 0.98), Ba and Sr (r = 0.86). Moderately positive correlation exists between the following:

Ni and Li (r = 0.79), Co and Mn (r = 0.75), Ni and Co (r = 0.72), Pb and Zn (r = 0.79), Pb and Cd (r = 0.74). A moderately negative correlation exist between V and Li (r = −0.04), Sr and Li (r = −0.03), Cu and Co (r = −0.08). A high correlation coefficient (nearly 1 or −1) means a good relationship between two variables, and a correlation coefficient around zero means no relationship. Positive values indicate a positive relationship while negative values of *r* indicate an inverse relationship [13].

Table 5. Trace metal concentration (μg/L) and basic statistics of groundwater in Mbonge-Kwakwa.

SN	Location	Li	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Sr	Cd	Ba	Pb
1	Bole II	3.54	0.40	1.61	167.98	401.38	15.28	28.40	8.60	92.14	0.09	43.36	0.32	172.00	2.25
2	Nake	3.02	1.25	2.19	93.25	346.91	2.45	13.81	23.64	168.50	0.18	69.35	0.34	195.67	6.37
3	Kwakwa	1.84	0.44	0.48	374.93	85.13	12.67	16.67	6.97	106.41	0.51	358.42	0.25	1640.18	1.33
4	Kumba	1.16	0.41	0.79	178.29	105.45	6.64	15.62	20.20	68.39	0.09	65.06	0.18	200.40	2.03
5	Kumba	0.24	1.43	1.54	15.37	88.29	1.25	4.49	7.12	56.05	0.05	102.54	0.13	15.05	1.55
6	Kumba	1.58	0.18	0.32	254.78	60.32	9.15	21.51	5.05	31.98	0.09	30.21	0.11	141.90	1.12
7	Kumba	0.76	0.17	0.22	86.25	52.29	4.36	7.35	3.10	15.11	0.10	12.49	0.05	59.03	0.87
8	Kumba	1.59	0.42	0.95	158.97	109.69	5.69	19.41	6.91	55.28	0.14	12.57	0.15	29.65	1.95
9	Kumba	1.60	1.00	10.25	268.04	176.20	5.80	16.66	13.32	96.63	0.68	110.15	0.28	76.08	3.82
10	Kumba	2.79	0.47	2.60	116.30	98.38	12.43	39.46	7.90	35.44	0.13	39.95	0.15	32.94	1.87
11	Kumba	1.74	0.63	0.98	520.70	263.54	9.55	7.42	8.21	53.08	0.05	8.07	0.12	9.03	2.17
12	Kumba	2.56	0.72	1.00	610.96	146.44	28.89	27.18	10.35	70.62	0.29	70.44	0.20	77.27	2.36
13	Kumba	0.92	1.63	1.05	37.28	369.14	1.87	5.19	18.62	67.31	0.10	9.98	0.14	4.26	3.13
14	Kumba	0.76	1.43	0.66	36.31	116.20	3.93	4.34	8.56	74.44	0.54	73.28	0.13	14.13	3.19
15	Kumba	1.32	0.89	0.98	134.78	173.51	2.91	7.52	18.57	80.32	0.20	30.46	0.28	21.42	5.15
16	Kumba	0.24	0.51	1.17	46.93	77.62	3.75	3.17	4.98	3.20	0.55	183.77	0.03	97.17	1.10
17	Kumba	0.62	0.45	0.97	51.87	106.89	2.80	4.53	5.86	22.07	0.07	18.00	0.04	10.70	0.94
18	Barombi N	0.47	0.24	0.52	25.77	51.13	1.66	2.28	3.62	9.73	0.03	5.00	0.04	4.50	1.00
19	Ediki	2.84	1.16	2.22	152.86	151.18	10.59	28.61	12.35	56.83	0.17	55.31	0.14	106.42	2.37
20	Mbalangi	2.00	0.68	1.00	36.46	102.45	1.64	4.77	7.94	39.38	0.12	23.96	0.05	16.77	1.04
21	Bombe	2.37	0.56	0.54	687.20	103.70	13.46	18.72	10.68	63.27	0.33	59.01	0.29	64.23	2.98
Min		**0.24**	**0.17**	**0.22**	**15.37**	**51.13**	**1.25**	**2.28**	**3.10**	**3.20**	**0.03**	**5.00**	**0.03**	**4.26**	**0.87**
Max		**3.54**	**1.63**	**10.25**	**687.20**	**401.38**	**28.89**	**39.46**	**23.64**	**168.50**	**0.68**	**358.42**	**0.34**	**1640.18**	**6.37**
Mean		**1.62**	**0.72**	**1.53**	**193.11**	**151.71**	**7.47**	**14.15**	**10.12**	**60.29**	**0.21**	**65.78**	**0.16**	**142.32**	**2.31**

3.10. Hierarchical Cluster Analysis HCA

The R-mode Cluster Analysis; hierarchical cluster analysis HCA performed on the groundwater of Kumba and environs area shows two clusters based on spatial similarities and dissimilarities. The trace metals fall in two clusters: Cluster one; (01) element Ba; soluble. Cluster two (13) non soluble elements divided into three classes; class one (06) As, Cd, V, Li, Pb, and Cr; less enriched. Class two (03) Co, Cu, Ni and Zn; enriched; Class two (04) Zn, Sr, Fe and Mn; more enriched (Figure 9).

3.11. Health Risk Assessment

Human health risk assessment was done to estimate the intensity, frequency, and duration of human exposures to an environmental contaminant. Exposure assessment was carried out by measuring the average daily dose ADD of the trace

Table 6. Correlation matrix of r values for trace metals and physico-chemical parameters in study area.

	Li	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Sr	Cd	Ba	Pb	Temp	PH	EC	TDS
Li	1																	
V	−0.04	1																
Cr	0.16	0.26	1															
Mn	0.42	−0.22	0.01	1														
Fe	0.48	0.44	0.17	0.02	1													
Co	0.61	−0.25	−0.03	**0.75**	0.07	1												
Ni	**0.79**	−0.21	0.20	0.38	0.11	**0.72**	1											
Cu	0.30	0.54	0.23	0.01	0.58	−0.08	0.1	1										
Zn	0.53	0.46	0.30	0.20	0.61	0.15	0.2	0.71	1									
As	−0.05	0.19	0.49	0.21	−0.14	0.13	0.0	0.02	0.26	1								
Sr	−0.03	0.01	0.10	0.17	−0.19	0.17	0.0	−0.07	0.29	0.65	1							
Cd	0.64	0.23	0.34	0.42	0.54	0.35	0.4	0.62	0.86	0.27	0.24	1						
Ba	0.14	−0.18	−0.10	0.23	−0.09	0.23	0.1	−0.05	0.36	0.35	0.86	0.29	1					
Pb	0.35	0.57	0.34	0.08	0.58	−0.07	0.1	0.82	**0.79**	0.22	−0.07	**0.74**	−0.1	1				
Temp	0.41	0.00	0.04	−0.12	0.17	−0.08	0.1	0.26	0.43	0.07	0.25	0.35	0.4	0.21	1			
PH	−0.13	0.46	0.37	−0.29	0.16	−0.26	−0.1	0.27	0.24	0.19	0.32	0.10	0.1	0.23	−0.16	1		
EC	−0.11	0.15	0.42	0.21	−0.25	0.13	0.0	−0.08	0.18	0.98	0.68	0.22	0.4	0.12	0.05	0.19	1	
TDS	−0.11	0.15	0.42	0.21	−0.25	0.13	0.0	−0.08	0.18	0.98	0.68	0.22	0.4	0.12	0.05	0.19	1	1

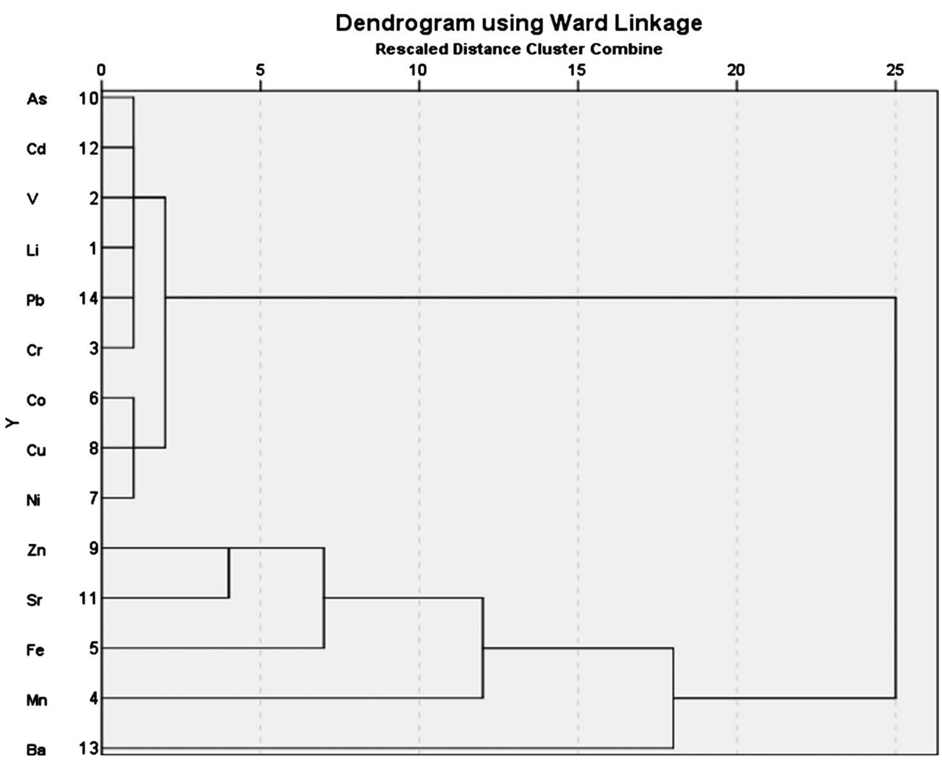

Figure 9. Dendrogram of trace metals in groundwater of the Akwa-Mundemba area made up of two clusters: cluster 1 (01) element Ba; soluble. Cluster two (13) non soluble elements divided into three classes; class one (06) As, Cd, V, Li, Pb, Cr; less enriched. Class two (03) Co, Cu, Ni and Zn; enriched; Class two (04) Zn, Sr, Fe and Mn; more enriched.

metals selected in Table 7. Carcinogenic and non carcinogenic risk were calculated from the ADD.

3.12. Average Daily Dose

ADD values ranged as follows; (Li) 8×10^{-6} to 1×10^{-4}, (V) 5.5×10^{-6} to 5.1×10^{-5}, (Cr) 7×10^{-6} to 3.2×10^{-4}, (Mn) 5×10^{-4} to 0.022, (Fe) 2×10^{-3} to 0.013, (Co) 4×10^{-5} to 9×10^{-4}, (Ni) 7×10^{-5} to 1.2×10^{-3}, (Cu) 1×10^{-4} to 7×10^{-4}, (Zn) 1.4×10^{-4} to 5×10^{-3}, (As) 1×10^{-6} to 2×10^{-5}, (Sr) 2×10^{-4} to 0.011, (Cd) 1×10^{-6} to 1×10^{-5}, (Ba) 1×10^{-4} to 0.052, (Pb) 3×10^{-5} to 2×10^{-4} as in Figure 10.

3.13. Hazard Qotient

HQ values ranged as follow; (V) 2.7×10^{-3} to 2.5×10^{-2}, (Cu) 2.4×10^{-3} to 1.8×10^{-2}, (Pb) 7.8×10^{-3} to 5.7×10^{-2}, (Zn) 3.3×10^{-5} to 1.7×10^{-2}, (Fe) 2.2×10^{-3} to 1.8×10^{-2}, (Mn) 7.6×10^{-2} to 1.59 as in Figure 11.

3.14. Carcinogenic Risk

CR for the carcinogenic elements; Cr, Cd, Ni and As are; (As) 2.2×10^{-4} to 4.4×10^{-4}, (Cd) 8.5×10^{-6} to 8.8×10^{-5}, (Cr) 3.9×10^{-4} to 1.8×10^{-2}, (Ni) 8.6×10^{-5} to 1.4×10^{-3} as in Figure 12.

Table 7. Parameters used for estimating exposure assessment [9].

Factor/parameter	Symbol	Units	Residential
Exposure duration	ED	Years	30
Exposure frequency	EF	Days in year	350
Average time	AT	Years	76.5
Body weight	BW	Kg	70
Ingestion rate	IR	L/day	2.2
Contaminant concentration	C	ug/L	Table 5

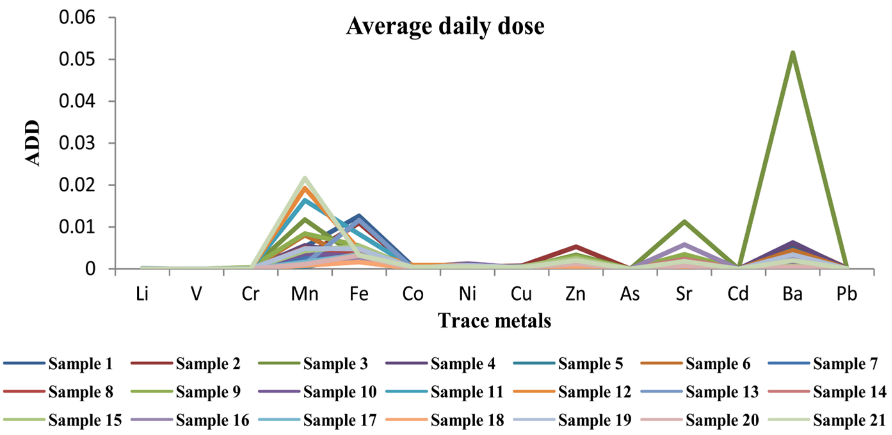

Figure 10. Average Daily Dose (ADD) of trace metals through water intake. All values are below toxic level in Kumba and envurons.

3.15. Hazard Index

HI is the cumulative sum of HQ. The values ranged between 0.07 and 1.59 for each of contaminant indicating no toxicity as in Figure 13.

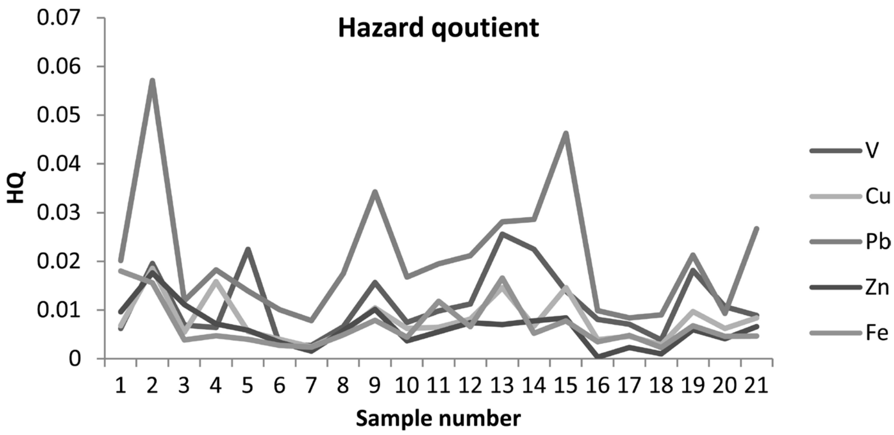

Figure 11. Hazard quotient (HQ) of trace metals through water intake. The value of Manganese in sample12 is above permissible levels in Kumba and environs.

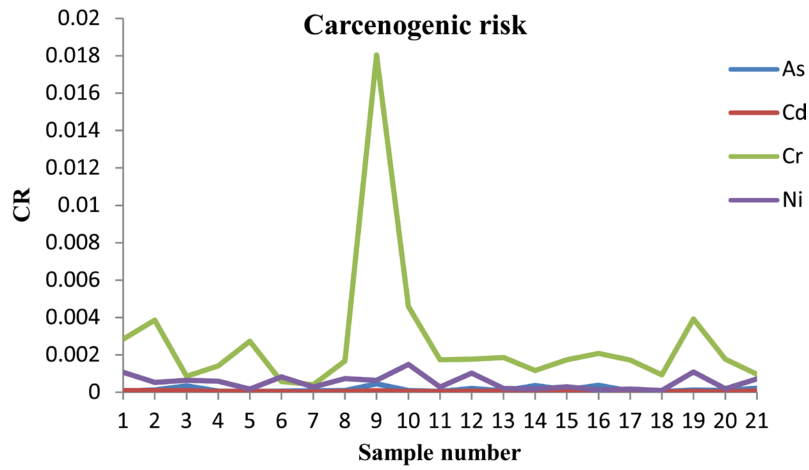

Figure 12. Carcinogenic risk (CR) of each contaminant.. All values are below toxic levels.

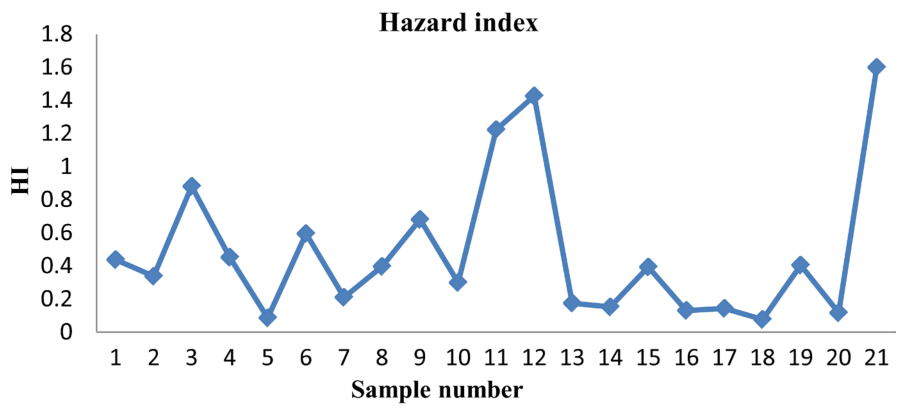

Figure 13. Non carcinogenic toxic risk index or hazard index (HI) of trace metals through water intake. The values in sample 11 (Kwakwa) is relatively high. All values are below toxic levels.

All the groundwater hazard risk indices; ADD, CR, HQ and HI were less than 1 but for sample 20 which had HI value greater than 1, thus the water is of significant health risk as shown in **Table 8**.

3.16. Pollution Evaluation Indices

Degree of contamination (DC)

The degree of contamination (DC) is used as reference of estimating the extent of metal pollution. The DC values in the groundwater ranged from −13.53 to 12.1 According to classification [15], 95.2% of the samples have degree of contamination factor < 10 which is indicative of low contamination whereas 4.8% of the samples have degree of contamination factor between 10 - 20 thus indicating moderate contamination.

Enrichment factor

Iron (Fe) was chosen as a stationary reference element to perform this calculation [22]. EF values < 2 indicate that the metal is entirely from crustal materials or natural processes; whereas EF values > 2 reveal that the sources are more likely to be anthropogenic [23]. The enrichment factors of trace metals in Kumba and environs were as shown in **Figure 14**, **Figure 15** and **Table 9**. The sequence of EF in the sediments was Ba > Co > Mn > Ni > Pb > Cd > Cr > As > Sr > Zn> Li > Cu > V. EF values in the study area are between 1.15 to 874.13 which is indicative of significant enrichment and that the source of these metals is from natural and anthropogenic processes. Barium and Cobalt are the most enriched elements in the study area; this could be attributed to agricultural wastes.

3.17. Ecological Risk Assessment

Ecological Risk Factor (Er) and Ecological Risk Index (RI)

Er and RI of the heavy metals in the investigated area are given in **Table 9** and **Figure 16** and **Figure 17**. All analyzed trace metals showed low potential ecological risk, it varied from −29.68 to 9.45 (Er < 40). RI of the studied trace metals ranged from −61.06 to −43.03. All the samples show low ecological risk index, this indicates low polluted according to [17].

Table 8. Summary Classification of health risk assessment carcinogenic and non-carcinogenic risk in Akwa-Mundemba.

INDEX	Range	Classification	Samples	(%)	Reference
CR	$>10^{-6}$ - $10^{-4}<$	Generally satisfactory	21	100	[15]
	$>10^{-4}$	Intolerable	-	-	
HQ	<1	Acceptable level (no concern)	18	85.7	[21]
	>1	No carcinogenic adverse effects	3	24.3	
HI	<1	Safe	18	85.7	[21]
	>1	Unsafe	3	24.3	

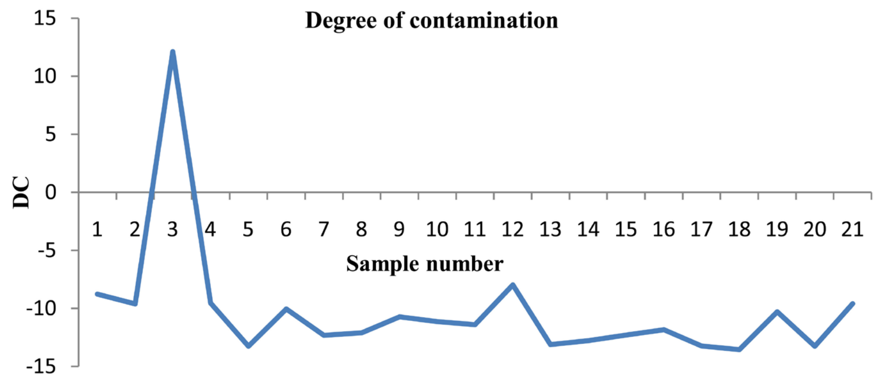

Figure 14. The degree of contamination for trace metals of groundwater in kumba and environs with sample 3 indicating moderate contamination.

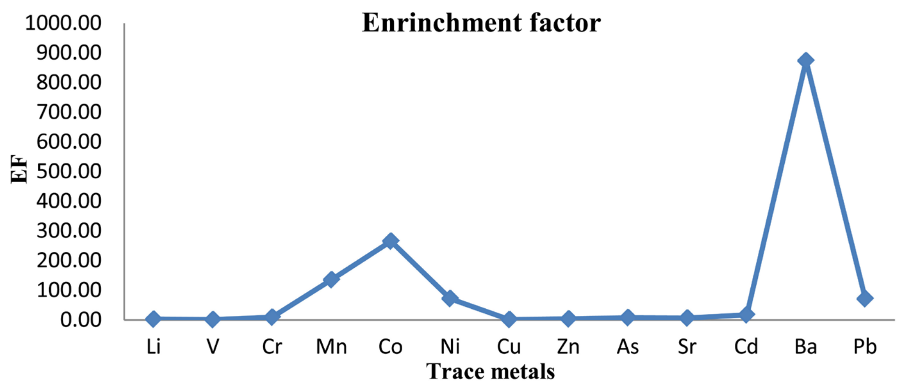

Figure 15. The enrichment factor for trace metal of groundwater in kumba and environs. Barium and Cobalt, are being enriched.

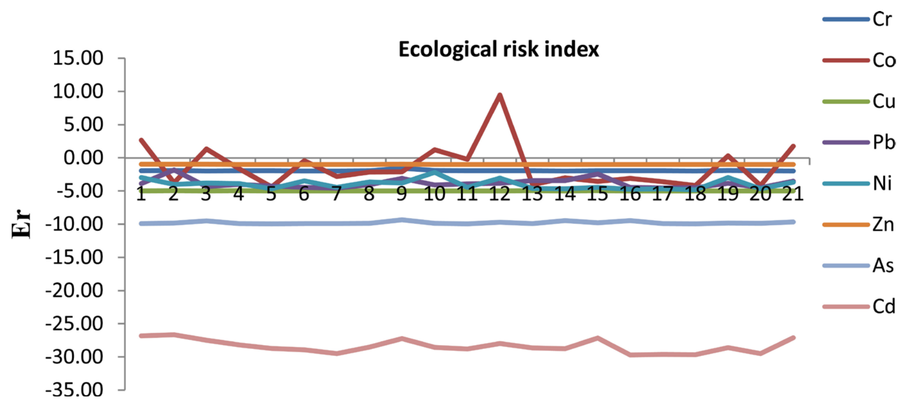

Figure 16. The Ecological risk factor Er for trace metal of groundwater in Kumba and environs.

Pollution Load Index (PLI)

This index is a quick tool in order to compare the pollution status of different places [24]. The values of Pollution Load Index are <1 which is indicative that there is no pollution. These results attributed principally to natural sources.

Geo-Accumulation Index Igeo

The geo-accumulation index Igeo is a quantitative measure of the degree of pollution in groundwater [25] as shown in **Table 9** presents the indices for the

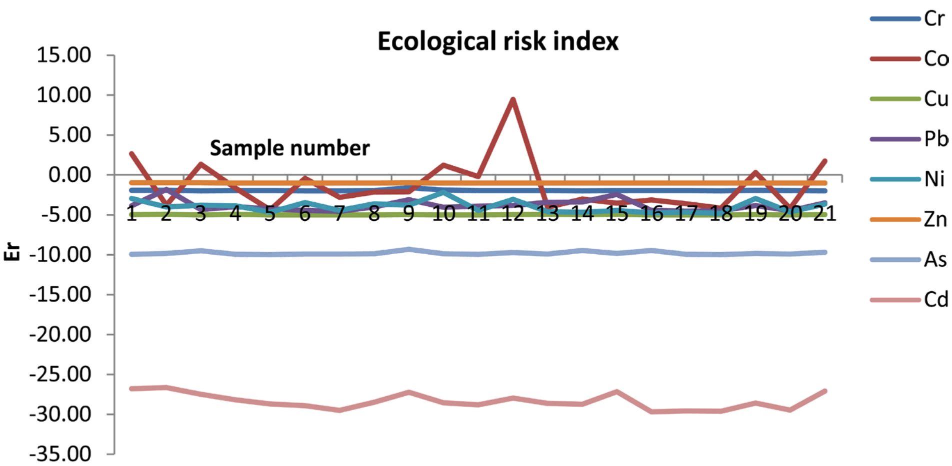

Figure 17. The Ecological risk index for trace metalof groundwater in Kumba and environs.

Table 9. The Geo-accumulation index (Igeo) of Kumba and environs groundwater.

SN	Li	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Sr	Cd	Ba	Pb
1	0.14	0.016	0.016	16.8	160.6	0.031	3.975	3.44	92.14	2E−04	34.7	2E−04	2.408	0.031
2	0.12	0.05	0.022	9.325	138.8	0.005	1.934	9.457	168.5	4E−04	55.5	2E−04	2.739	0.089
3	0.07	0.018	0.005	37.49	34.05	0.025	2.333	2.787	106.4	0.001	287	2E−04	22.96	0.019
4	0.05	0.016	0.008	17.83	42.18	0.013	2.187	8.082	68.39	2E−04	52.1	1E−04	2.806	0.028
5	0.01	0.057	0.015	1.537	35.31	0.002	0.629	2.849	56.05	9E−05	82	8E−05	0.211	0.022
6	0.06	0.007	0.003	25.48	24.13	0.018	3.011	2.019	31.98	2E−04	24.2	7E−05	1.987	0.016
7	0.03	0.007	0.002	8.625	20.92	0.009	1.028	1.238	15.11	2E−04	9.99	3E−05	0.826	0.012
8	0.06	0.017	0.009	15.9	43.88	0.011	2.718	2.764	55.28	3E−04	10.1	9E−05	0.415	0.027
9	0.06	0.04	0.102	26.8	70.48	0.012	2.333	5.326	96.63	0.001	88.1	2E−04	1.065	0.053
10	0.11	0.019	0.026	11.63	39.35	0.025	5.524	3.158	35.44	3E−04	32	9E−05	0.461	0.026
11	0.07	0.025	0.01	52.07	105.4	0.019	1.039	3.284	53.08	1E−04	6.45	7E−05	0.126	0.03
12	0.1	0.029	0.01	61.1	58.58	0.058	3.805	4.139	70.62	6E−04	56.4	1E−04	1.082	0.033
13	0.04	0.065	0.01	3.728	147.7	0.004	0.726	7.448	67.31	2E−04	7.98	8E−05	0.06	0.044
14	0.03	0.057	0.007	3.631	46.48	0.008	0.608	3.423	74.44	0.001	58.6	8E−05	0.198	0.045
15	0.05	0.035	0.01	13.48	69.41	0.006	1.053	7.428	80.32	4E−04	24.4	2E−04	0.3	0.072
16	0.01	0.021	0.012	4.693	31.05	0.008	0.444	1.99	3.199	0.001	147	2E−05	1.36	0.015
17	0.02	0.018	0.01	5.187	42.76	0.006	0.635	2.342	22.07	1E−04	14.4	3E−05	0.15	0.013
18	0.02	0.01	0.005	2.577	20.45	0.003	0.32	1.448	9.729	7E−05	4	2E−05	0.063	0.014
19	0.11	0.046	0.022	15.29	60.47	0.021	4.005	4.941	56.83	3E−04	44.2	9E−05	1.49	0.033
20	0.08	0.027	0.01	3.646	40.98	0.003	0.668	3.177	39.38	2E−04	19.2	3E−05	0.235	0.015
21	0.09	0.023	0.005	68.72	41.48	0.027	2.621	4.273	63.27	7E−04	47.2	2E−04	0.899	0.042
Min	**0.01**	**0.007**	**0.002**	**1.537**	**20.45**	**0.002**	**0.32**	**1.238**	**3.199**	**7E−05**	**4**	**2E−05**	**0.06**	**0.012**
Max	**0.14**	**0.065**	**0.102**	**68.72**	**160.6**	**0.058**	**5.524**	**9.457**	**168.5**	**0.001**	**287**	**2E−04**	**22.96**	**0.089**
Mean	**0.06**	**0.029**	**0.015**	**19.31**	**60.68**	**0.015**	**1.981**	**4.048**	**60.29**	**4E−04**	**52.6**	**1E−04**	**1.993**	**0.032**

quantification of trace metal accumulation in the Akwa-Mundemba. The values range as in Table 4. Groundwater is Unpolluted to moderately polluted by Pb, V, Cr, Co, As, Cd, Pb; while it is Extremely polluted by Mn, Fe, Ni, Cu, Sr, Zn, Ba (Figure 18).

The results of pollution evaluation indices are presented in Table 10.

4. Conclusions

The groundwater in Kumba and environs presents no pollution risks or hazards.

The degree of contamination and contamination factors such as the ER, EF, PLI and Igeo had low values of trace metals indicating that, the groundwater is unpolluted with Barium being the most enriched metal. Thus, from health risk indices and pollution evaluation indices of trace metals, the groundwater in Kumba and environs area is safe for drinking.

The enrichment factors show that the sources of the trace metals are from geogenic and anthropogenic processes.

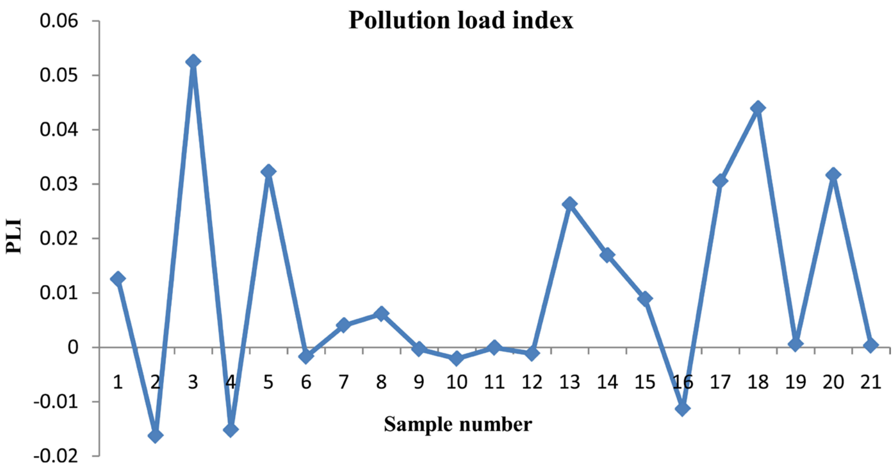

Figure 18. The Pollution load index for trace metalof groundwater in Kumba and environs.

Table 10. Summary Classification of Kumba and environs groundwater based on pollution evaluation indices.

INDEX	Range	Classification	SN	%
DC	<10	low degree of contamination factor	20	95.2
	10 - 20	moderate degree of contamination	1	4.8
EF	2- 5	Moderate enrichment	2	9.52
	5 - 20	Significant enrichment	10	47.62
	20 - 40	Very high enrichment	9	42.86
Er	<40	Low potential risk	21	100
RI	<150	Low ecological risk	21	100
PLI	<1	No pollution	21	100
Igeo	0 - 1	Unpolluted to moderately polluted by	Pb, V, Cr, Co, As, Cd, Pb	
	>5	Extremely polluted by	Mn, Fe, Ni, Cu, Sr, Zn, Ba	

The severity of metal toxicity is governed by several factors, such as dose, nutrition, age, and even life style. Therefore, these low trends might not guarantee the complete absence of human health risks. Generally, from risk assessment on trace metals using risk indices in the analyzed groundwater samples might not cause any health risk. However, due to an increasing level of environmental pollution that might be imposed by increasing human activity in this area, groundwater sources might become a potential sink of contaminants; this is significant reason that makes constant monitoring, implementation and treatment of groundwater for drinking purposes necessary.

The trace metal concentrations in the study are within WHO permissible limits except that of Barium and Manganese which are above permissible limits.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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