

Assessing the Trace Metal Content of Groundwater in the Bakassi Peninsular, Onshore Rio del Rey, Akwa-Mundemba, Cameroun

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Abstract

The present work assesses the trace metal content in groundwater from Akwa-Mundemba, Bakassi Peninsular in Cameroon. 12 groundwater samples were analyzed using Inductively Coupled Plasma Mass Spectroscopy ICP-MS. 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 ($2.5E-07$ to 0.2) carcinogenic risks CR ($2.1E-06$ to $9.9E-04$) and the non-carcinogenic risk hazard quotient HQ ($5.7E-04$ to 0.78) which yields the hazard indices HI (0.1 - 0.78), and six trace metal pollution indices; Degree of contamination DC (-13.53 to -11.02), Enrichment factor EF (0.26 - 35.47), Ecological risk factor Er (-29.92 - 7.04), Potential ecological risk index RI (-61.2 - 43.43), Pollution load index PLI (-0.01 - 0.04) and Geo-accumulation index Igeo ($4.8E-09$ - 3.0). From health risk indices and pollution evaluation indices on trace metals, the groundwater in Akwa-Mundemba area is safe for drinking. The enrichment factors show that the sources of the trace metals are from geogenic and anthropogenic processes. Arsenic, Lead and Vanadium are enriched although they are 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.

Keywords

Trace-Metals, Pollution Indices, Hazard Indices, Bakassi-Peninsular, Rio-del-Rey, Cameroun

1. Introduction

Akwa-Mundemba area is found between, 4.450N - 4.955N and 8.500E - 8.950E in the Bakassi Peninsular, Ndian Division of the South West Region in Cameroon as in **Figure 1**. Groundwater is the main resource for drinking in the area through springs, handdug wells and boreholes. The study area has a surface area of 1.557 kilometres squares. Mundemba shares boundaries with Eyumojock in

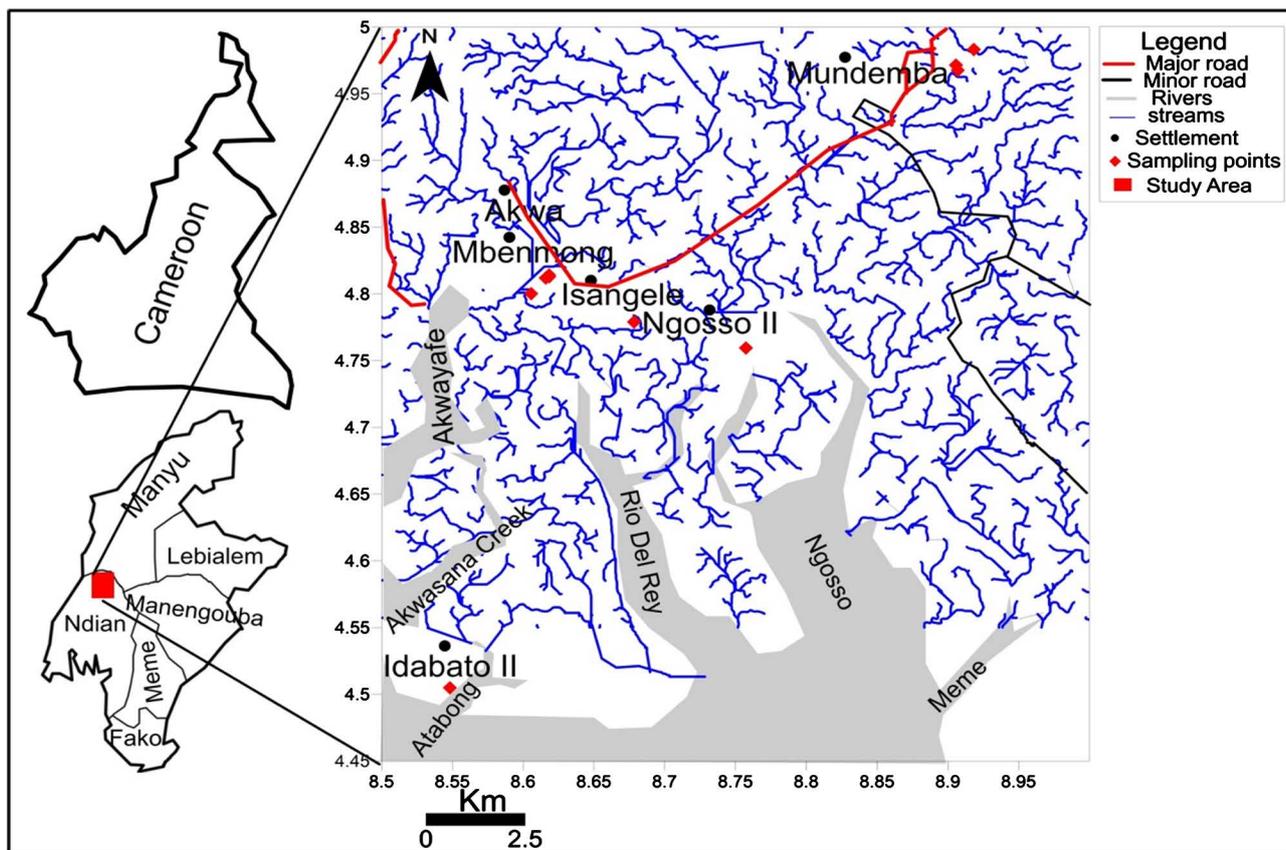


Figure 1. Location map for measurements and sample collection.

North, Isangele and Ekondo Titi in the South, Toko, Konye and Dikome-Balua in the East and Nigeria in the West. It is a gateway to Nigeria and other countries.

This area is an agro-industrial zone of fishing, palm oil, rubber and banana plantations, all of which are exported and dependent on groundwater. There are petroleum companies exploiting oil off-shore in the area. The presence of industries has led to unprecedented population growth and urbanization around this area resulting in a high demand for water that has now exceeded supply. 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 are high (Mehri & Marjan, 2013).

Trace metals are chemical components found in low concentrations, in mass fractions of ppm or less, in water, organisms and soil (Akoachere et al., 2019). 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 (mg/L) like Cd 0.01, Pb 0.10 and Cu 0.050 (Verma & Dwivedi, 2013). 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 (Akoachere et al., 2019). 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.

1.1. Climate

This area has an equatorial climate with two main seasons: the dry and the wet seasons. The dry season is usually very short and runs from November to February while the wet season is long and it's between March to October. The mean monthly temperature ranges from 23°C to 30°C (Cameroon Pamol Plantation, Cameroon, 2005-2008).

1.2. Relief

The study area is composed of a stretch of hilly topography. It is made of gentle slopes gradually increasing from the south west coast of river Ndian to the undulating slopes of the Rumpi Hills forest reserve in the south west, stretching right up to Toko sub division. Another stretch of undulating hilly topography is found in the south east of the area, around the northern part of the Rumpi forest reserve. The highest point here is a hill with altitude of 505 m (Mundemba Monographic Study, 2010).

1.3. Hydrology

The Akwa-Mundemba area is characterized with numerous streams, spring and major rivers; the Akwa Yafe River, Dibonda and the Mundemba rivers. Most of the rivers and streams take their rise from the Rumpi hills and the northern part of the Korup national park (KNP). Rivers and streams that take their rise from the Rumpi hills and flows towards the northern section of the proposed council forest while those that take their rise from the northern part of the KNP flow in a southern direction of the park. The streams combine to form the Mana and Mbo's rivers that finally drain into river Ndian and the Atlantic Ocean while the main stream Mossambi converges with river Lokeri and drains into the Dibonda river, which empties into the Atlantic Ocean.

1.4. Geology

Cameroon's geology is made of different rock types.

These are:

- 1) Precambrian basement rocks covering about 77% of Cameroon and underlie;

2) Sedimentary rocks covering 9% are of Cretaceous to the Cenozoic Era intruded in some areas by;

3) The Tertiary to recent volcanics covering 10% found generally along the Cameroon Volcanic Line (CVL);

4) Over a, b and c, above along major river channels, deltas and seashores are recent alluvium that make up some 4%.

Bakassi Peninsula is found in the Rio del Ray basin (Coastal basin) which is one of the Equatorial Atlantic marginal basins in the Gulf of Guinea, covering 2500 sq-km and dipping ocean-wards with about 6000 m thick of sediments ranging from Cretaceous to Recent. The basin proper is bordered to the west and northwest by the contemporaneous Niger Delta Basin, limited to the south by the Island of Bioko, the north by the Rumpi Hills and to the east by the Cameroon Volcanic Line (CVL) separating the Rio del Ray basin from the Douala Basin.

The Rio del Ray basin and the Douala basin are genetically related and were linked together constituting one composite basin, which was itself attached to the Niger Delta in Nigeria. There are four Formations of the Rio del Ray basin; Akata, Agbada, Benin and the Isongo formations averaging a depth of 2.5 km.

The Akata Formation is about 600 m - 6000 m thick. The sands are continental slope channel-fills and turbidities.

The Agbada Formation overlies the Akata Formation and consists of interbedded sand and shales with thickness of about 300 m - 4500 m. The coarse clastic beds are the oil reservoirs of up-to-date discovered oilfields.

The Benin Formation is the topmost Tertiary sequence of the Niger Delta and continues eastwards into the Rio del Ray basin as a fringe zone of shales diapirs, sandy clays, dark-green sandstones, lignites and fragments of volcanic rocks. The Benin Formation has a thickness of about 1890 m - 2300 m at the center.

The Isongo Formation is encountered mostly south-east of the Rio del Ray basin and represent a mixed phase of marine shales and fan sands.

The Formations in the Rio del Ray basin that outcrop onshore are Aptian to Albian Mundeck, coarse fluvial sandstone and the late cretaceous Mungo and Logbaba, shallow marine limestones, sandstones and shales which are overlain unconformably by Tertiary non marine sands and silts. Offshore the sequence above the unconformity is Eocene to recent, the Akata Formation, diachronous pro-deltaic shales are overlain by the Agbada, deltaic front sandstones, shales and the Benin, fluvial sands. The Rio del Ray basin also contain some features of the Cameroon Volcanic Line (CVL), an alignment of volcanic massifs trending north-south from the island of Pagalu to lake Tchad, consisting of a hosts and grabens and is an example of intraplate volcanism (Fitton, 1980; Fitton & Dunlop, 1985; Halliday et al., 1988, 1990). The CVL is a "Y" shape long chain of Tertiary to Recent Volcanic complexes with a general NE-SW orientation and spreads from the South Atlantic into the interior of Africa. Amongst the 60 volcanic craters that litter the CVL, Mount Cameroon is the most active. The CVL extends more than 900 km across Cameroon from Bui and Adamawa plateau in

the north of mount Cameroon and Equatorial Guinea (Poudjom Djomani et al., 1997), it then continues for another 700 km through the Atlantic island of Principe, Sao Tome and Palagu (Ubangoh, 1998). The CVL was initiated by an upwelling mantle plume since the onset of the continental breakup in the early cretaceous. It generally consists of basalts to ryholite nephelinites, phenolites and trachytes with volcanic rocks found within the volcanoes (Halliday et al., 1988). The continental volcanoes are Mount Fako, Rumpi hills, Manengouba, Bambutus, Oku and the volcanic rocks of Kapsiki plateau and the Benue valley (Nono et al., 2004). The oceanic part is made up of Annabon, Sao-Tome, Bioko and Principi (Ngako et al., 2006). The continental sector of the CVL seems to follow old suture zones between two seismically and paleomagnetically distinct lithospheric blocks (Fairhead & Binks, 1991; Smith & Livermore, 1991). The major rock formations in Bakassi Peninsular onshore around Mundemba are; granite, gneiss, metasediments (Cretaceous; Tertiary sediments), volcanics, and Recent alluvium as in **Figure 2**.

The Cretaceous-Tertiary sediments vary according to the environment of deposition and are essentially clastic, consisting of sands, sandstone, and conglomerates with subsidiary clays, shales, marls and lignites outcropping beyond the southern catchments' limits with a thickness of about 68 meters. The Tertiary-Quaternary basaltic lavas associated with the Cameroon Volcanic Line, as part of the major Fouban shear zone, intruded the sediments during the Miocene (Dumort, 1968). This magmatic activity resulted in extensive lava flows that formed the Rumpi hills in the north and intruded the sediments in the south. These extrusive events lapsed for sufficient time allowing a substantial

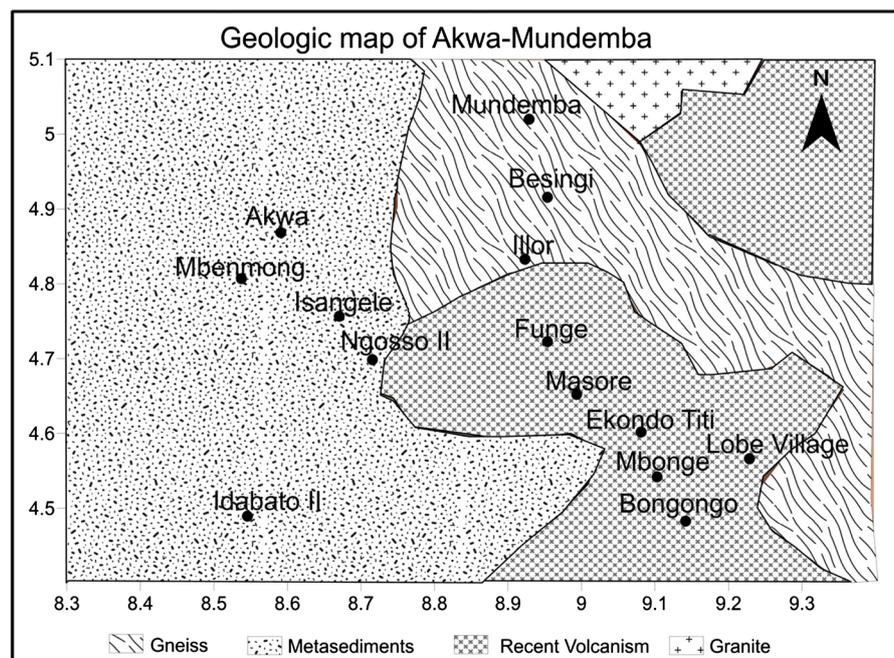


Figure 2. Geologic map of study area made up of four rock types; gneiss, metasediments, recent volcanism and granites.

layer of ash and basaltic lava flows to become interbedded with the extensive alluvium, deltaic and lacustrine deposits and in the study area columnar basalts are common intrusive. Recent alluvium is being deposited along the present coastline and margins of the delta of the Akwa Yafe River.

1.5. Hydrogeology

The aquifer(s) in this area are heterogeneous intercalation of fluvio-deltaic and marines conglomerates, sands, sandy clays, lateritic silts, silty clays, clayey sands, shales and marl lenses. Also the fractured gneisses and granites constitute good aquifers in some areas around Toko, Mundemba Town etc.

The study aims to improved knowledge on the occurrence of trace metals in groundwater in Akwa-Mundemba, which will provide information on the concentration ranges, act as basis for future regulations on trace metals in drinking, provide estimates of the contribution of groundwater to overall trace metal intake, provide baseline on trace metals if challenges arise in the future, estimate the health hazard and pollution indices of trace metals in groundwater of Akwa-Mundemba area.

2. Materials and Methods

2.1. Sample Collection, Pre-Treatment and Chemical Analysis

Twelve groundwater samples were collected from 12 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](#).

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 $\text{pH} < 2$ 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.

2.2. 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 ([Paustenbach, 2002](#)) as shown in [Table 2](#).

2.3. Exposure Assessment

This is the process of measuring or estimating the intensity, frequency and duration of human exposures to an environmental agent ([Paustenbach, 2002](#)). The

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 transmission to 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 (Akoachere et al., 2019).

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.

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 was calculated using

Equation (1) (Hu et al., 2012).

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

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 (Hu et al., 2012).

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 affect 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 (USEPA, 2012).

2.6. Carcinogenic Risk Assessment

Carcinogenic risks were 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 (Lushenko, 2010). 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) (Lushenko, 2010; Koki et al., 2015; Kamunda et al., 2016).

$$CR = ADD \cdot SF \quad (2)$$

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 $[\text{mg}/\text{kg}/\text{d}]^{-1}$.

2.7. Non Carcinogenic Risk Assessment

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) (Song et al., 2015).

$$HQ = \frac{ADD}{RfD}, \quad (3)$$

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 (Kim et al., 2011).

2.8. Hazard Index (HI)

It is the toxic risks due to all the potentially hazardous substances present in the same media simultaneously (Kolluru et al., 1996). 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) (Song et al., 2015).

$$HI = \sum_{i=1}^n HQ_i \quad (4)$$

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 (E_r), potential ecological risk index (RI), pollution load index (PLI) and geo-accumulation index (I_{geo}) were used to evaluate the pollution potential of the study area as in Table 3.

Table 3. Formulae for calculation of pollution indices.

Trace element pollution indices	Formulae	Reference
Degree of contamination	$DC = \sum_{i=1}^n C_f^i$	(Edet & Offiong, 2002)
Enrichment factor	$ER = \frac{(C_i/C_{ie})_{\text{sample}}}{(C_i/C_{ie})_{\text{background}}}$	(Zhang et al., 2007)
Ecological risk factor	$E_r^i = T_r^i \times C_f^i$	Hakanson (1980)
Ecological risk index	$RI_i = \sum_{i=1}^n E_r^i$	Hakanson (1980)
pollution load index	$PLI = \sqrt[n]{C_{f1} \times C_{f2} \times \dots \times C_{fn}}$	(Harikumar et al., 2009)
Geo-accumulation index	$I_{geo} = \log_2 [C_i / (1.5C_{ni})]$	(Ji et al., 2012)

3. Results and Discussion

Physicochemical Parameters

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

3.1. Water Level Fluctuations

Depth-to static water level (m) of groundwater ranged from: 0 - 0.77 as in **Figure 3**. Areas with low depths to static water levels are susceptible to pollution if the wells are not appropriately constructed and protected.

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)	26.2	30.6	28.3
PH	5.2	9.1	7.0
EC (mS/cm)	1.2	1504	231.3
TDS (mg/L)	0.8	1007.7	155.0

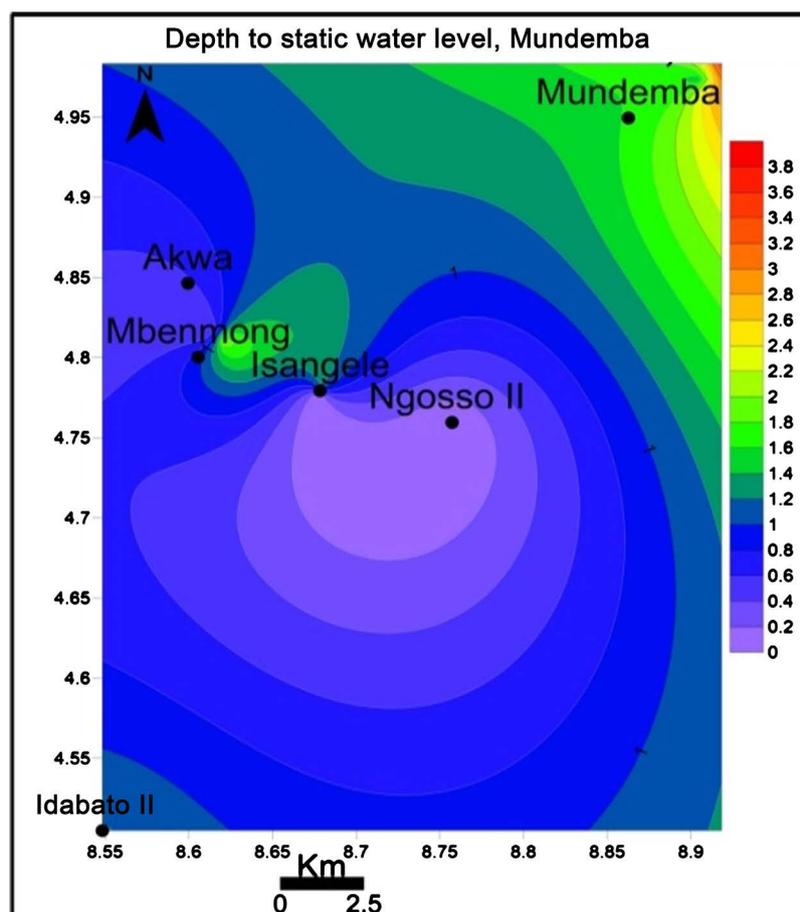


Figure 3. Depth to static water level; high values are at Mundemba whereas low values are at Ngosso II, Akwa, Idiabato II and Isangele.

3.2. Groundwater Flow Direction

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

3.3. Temperature

Temperature values of groundwater ranged from: 26.2°C - 30.6°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.

3.4. pH

The pH value of most of the groundwater samples in the study area ranged from 5.2 - 9.1 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 alkaline.

3.5. Electrical Conductivity

The EC ranged from 12 - 15,040 mS/m as in **Figure 7**. The high electrical

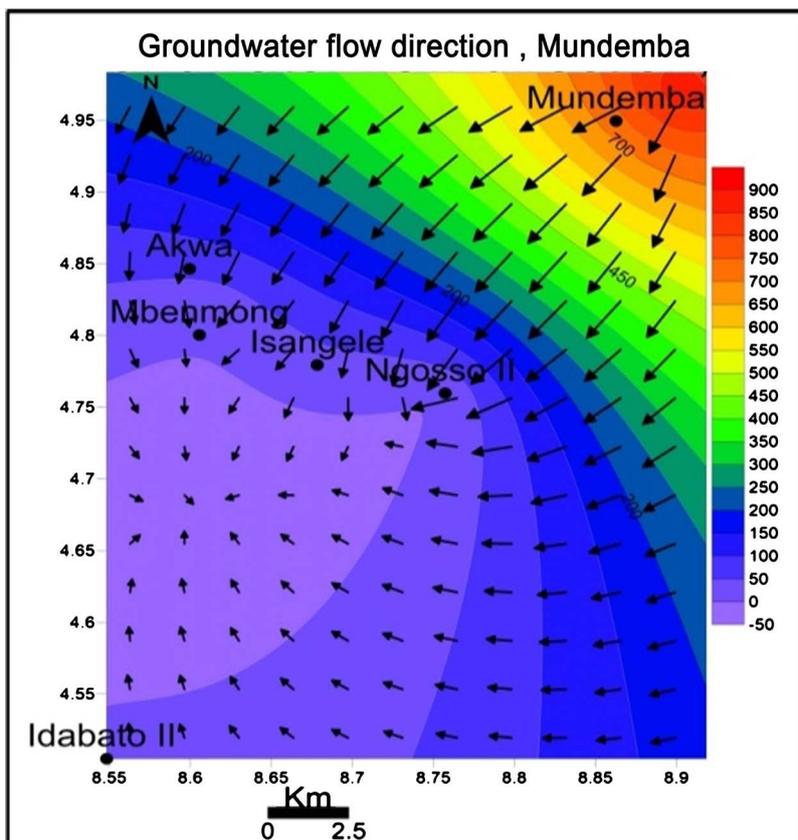


Figure 4. Groundwater flow direction in study area indicating that water flows towards the Southwestern part of the study area.

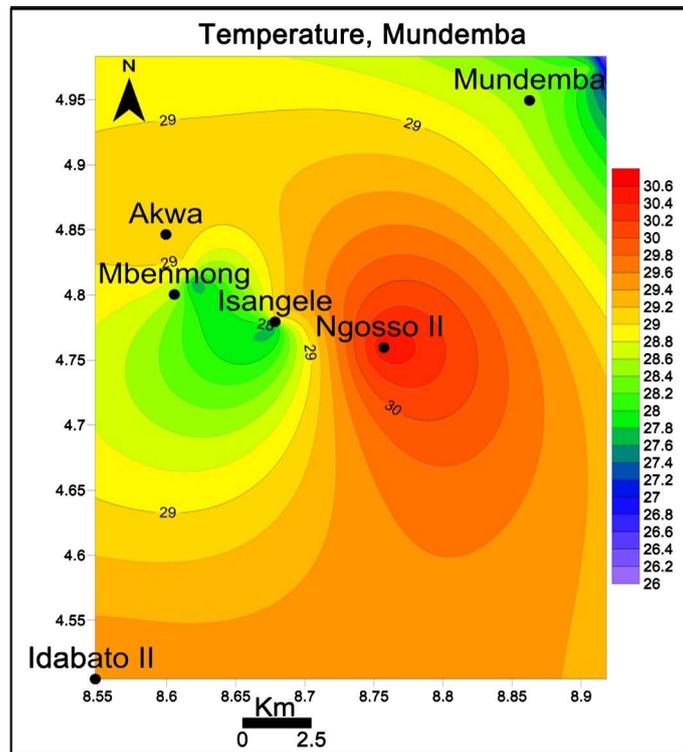


Figure 5. Spatial variation of groundwater temperatures; Temperatures are generally higher at Ngosso II and Idabato II while low values are at Isangele.

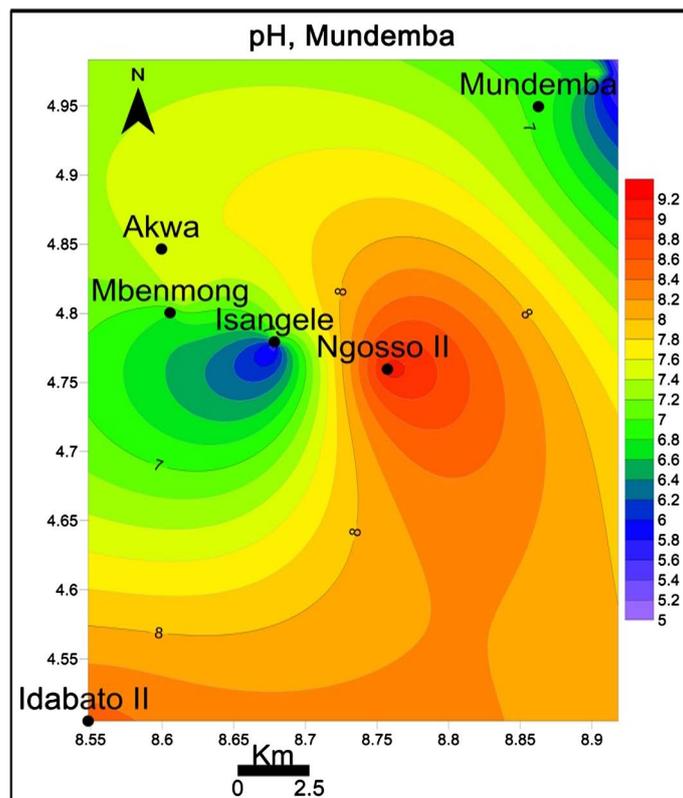


Figure 6. Spatial variation of pH; High pH values are at Ngosso II and Idabato II while low values are at Isangele.

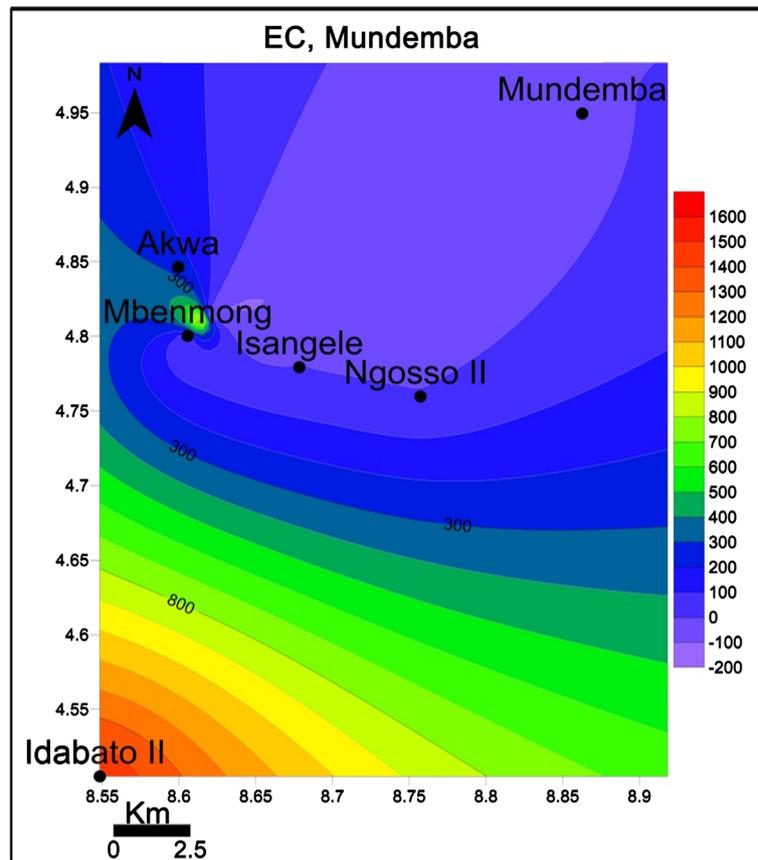


Figure 7. Spatial variation of Electrical Conductivities (mS/m); EC is at maximum at Idiabato II and minimum at Isangele and Mundemba.

conductivity is due to high solute concentration in groundwater. This high EC is characteristic of high saline waters with $EC > 2250$, high concentration Na^+ , HCO_3^- and CO_3^{2-} ions characterized by high pH.

3.6. Total Dissolved Solids

The total dissolved solids ranged from 0.80 - 1007.7 mg/L as in **Figure 8**. A TDS of 500-1500 indicates water is slightly saline.

3.7. Summary of Trace Metal Concentration

The results for twelve samples of trace metal analysis ICP-MS are presented in **Table 5**. The concentrations of fourteen trace metals; Zn, Pb, Co, Cu, Cr, Mn, Sr, Cd, V, Fe, Ni, As, Li, Ba, Mn, and Pb were evaluated since they were of significance. All concentrations of these trace metals are below the WHO (2011) allowable limits except Fe which had concentration 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 $\mu\text{g/L}$: Fe (122631), Zn (334.2), Sr (88.9), Mn (47.84), Cu (19.21), Ba (18.6), Ni (5.18), Li (2.23), Pb (2.21), As (1.53), Co (1.5), Cr (0.56), V (0.32) and

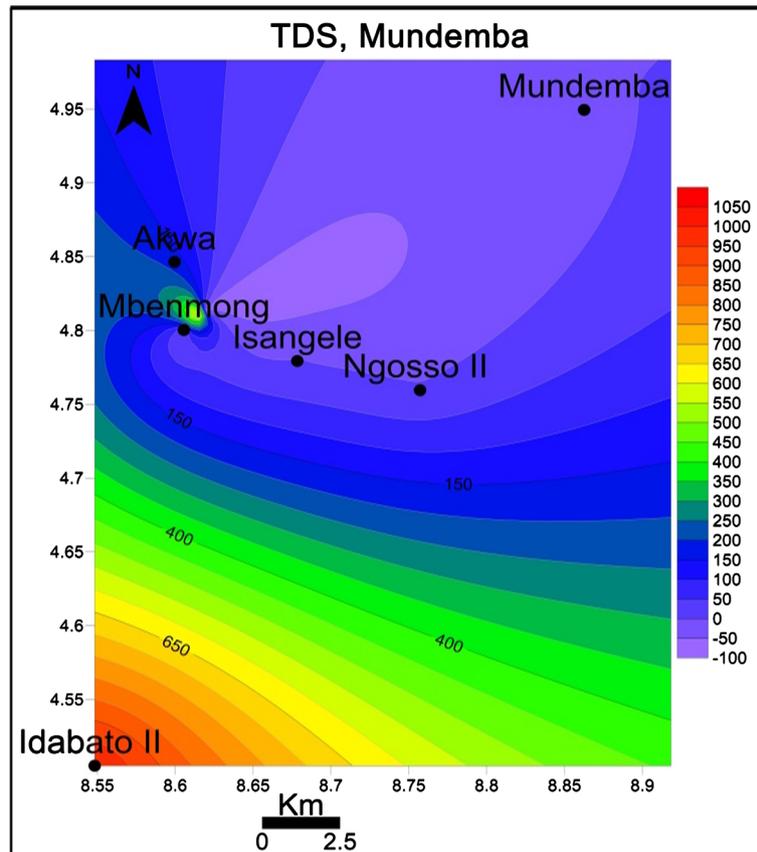


Figure 8. Spatial variation of total dissolved solids mg/L; TDS is at maximum at Idiabato II and minimum at Isangele and Mundemba.

Table 5. Trace metal concentration ($\mu\text{g/L}$) and basic statistics of groundwater in Akwa-Mundemba.

SN	Location	Li	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Sr	Cd	Ba	Pb
1	Idabato II	12.11	0.60	0.30	53.38	99.22	4.12	0.32	98.54	5.47	17.04	754.41	0.01	27.29	0.22
2	Ngosso II	0.64	0.61	0.87	47.75	229.76	0.55	2.47	6.30	20.29	0.36	24.57	0.10	1.77	0.96
3	Akwa-1	0.71	0.19	0.41	13.42	6516.33	0.54	2.45	4.77	23.00	0.19	11.13	0.06	6.29	1.30
4	Akwa-2	1.92	0.15	0.33	84.36	1245.06	1.06	2.73	10.39	470.37	0.08	76.84	0.08	91.30	2.68
5	Akwa-3	1.99	0.11	0.14	120.26	2136.29	2.14	0.69	1.65	7.72	0.15	102.91	0.02	13.95	0.81
6	Mbenmong	2.00	0.07	0.24	9.73	155.13	0.24	0.77	40.96	41.04	0.01	6.89	0.03	7.35	3.14
7	Isangele-1	1.78	0.04	0.06	129.64	3654.56	1.81	10.41	10.90	3008.02	0.03	8.51	0.04	6.51	0.32
8	Isangele-2	0.80	0.17	0.57	16.59	190.52	0.62	2.18	3.53	54.09	0.11	7.00	0.07	20.97	1.02
9	Mundemba-1	1.32	0.60	1.43	20.19	165.82	1.78	13.19	17.63	123.22	0.09	16.61	0.97	17.34	4.31
10	Mundemba-2	1.83	0.53	1.04	16.67	137.48	1.49	10.06	15.10	89.14	0.09	13.99	0.34	10.17	4.30
11	Mundemba-3	0.18	0.38	0.67	41.26	93.06	2.08	9.81	10.62	68.02	0.09	26.84	0.27	9.09	3.81
12	Mundemba-4	1.48	0.40	0.58	20.89	92.53	1.54	7.13	10.15	100.00	0.09	17.06	0.45	11.16	3.66
	Min	0.18	0.04	0.06	9.73	92.53	0.24	0.32	1.65	5.47	0.01	6.89	0.01	1.77	0.22
	Max	12.11	0.61	1.43	129.64	6516.33	4.12	13.19	98.54	3008.02	17.04	754.41	0.97	91.30	4.31
	Mean	2.23	0.32	0.56	47.84	1226.31	1.50	5.18	19.21	334.20	1.53	88.90	0.20	18.60	2.21
	WHO limit	200	200	50	400	2000	10	70	2000	5000	10	400	3	70	10

Cd (0.2). The trace metal with the highest concentration is Fe with a maximum value of 651,633 µg/L detected at Akwa.

3.8. 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.

Positive values indicate a positive relationship while negative values of r indicate an inverse relationship. A very strong positive correlation exists between the following trace metals; Li and Cu, As and Li, Sr and Li, Sr and Co, As and Cu, Sr and Cu, Sr and As, Cd and Cr, PH and temperature, TDS and EC. A strong positive correlation exists between the following; Co and Li, EC and Li, TDS and Li, Cr and V, As and Co, Cd and Ni, As and EC. A negative correlation exists between the following; V and Mn, Mn and Cr, Zn and Cr, Cd and Mn, TDS and Ni.

3.9. Hierarchical Cluster Analysis HCA

The R-mode cluster analysis; hierarchical cluster analysis HCA, performed on

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

	Li	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Sr	Cd	Ba	Pb	Temp	pH	EC	TDS
Li	1																	
V	0.32	1																
Cr	-0.26	0.75	1															
Mn	0.11	-0.39	-0.56	1														
Fe	-0.18	-0.49	-0.42	0.27	1													
Co	0.78	0.39	-0.10	0.34	-0.19	1												
Ni	-0.34	0.29	0.59	-0.05	-0.11	0.10	1											
Cu	0.94	0.34	-0.17	-0.10	-0.29	0.66	-0.29	1										
Zn	-0.07	-0.42	-0.38	0.64	0.37	0.07	0.37	-0.12	1									
As	0.98	0.40	-0.19	0.04	-0.18	0.78	-0.34	0.92	-0.13	1								
Sr	0.98	0.36	-0.24	0.13	-0.17	0.81	-0.38	0.89	-0.14	0.99	1							
Cd	-0.23	0.54	0.83	-0.38	-0.32	0.07	0.75	-0.15	-0.17	-0.22	-0.25	1						
Ba	0.17	-0.16	-0.16	0.25	-0.10	0.06	-0.21	0.07	-0.02	0.11	0.19	-0.10	1					
Pb	-0.38	0.29	0.63	-0.53	-0.43	-0.19	0.59	-0.20	-0.33	-0.40	-0.41	0.72	0.05	1				
Temp	0.35	0.11	-0.36	0.28	0.08	0.11	-0.46	0.30	0.15	0.36	0.35	-0.64	-0.35	-0.64	1			
pH	0.41	0.15	-0.33	0.32	0.22	0.15	-0.56	0.32	-0.02	0.43	0.45	-0.62	0.02	-0.58	0.86	1		
EC	0.71	0.19	-0.24	-0.13	0.40	0.46	-0.40	0.65	-0.17	0.76	0.74	-0.29	0.00	-0.44	0.28	0.46	1	
TDS	0.71	0.19	-0.24	-0.13	0.40	0.46	-0.40	0.65	-0.17	0.76	0.74	-0.29	0.00	-0.44	0.27	0.46	1.0	1

the groundwater of the Akwa-Mundemba area shows two clusters based on spatial similarities and dissimilarities as shown in **Figure 9**. The trace metals fall in two clusters: Cluster one (1) Fe, soluble. Cluster (2), slightly soluble, is divided into two classes; class (1) Zn, immobile. Class (2) further divided into two subclasses; subclass (1) Sr, slightly mobile. Subclass two V, Cd, Cr, Co, Pb, Li, As, Ni, Cu, Ba and Mn; mobile under present EC, pH and temperature conditions which is indicative that they originate from different parent rocks.

4. Health Risk Assessment

Human health risk assessment was done to estimate the intensity, frequency, and duration of human exposures to environmental contaminants using the parameters in **Table 7**. Exposure assessment was carried out by measuring the average daily dose ADD of the trace metals selected in **Table 5**. Carcinogenic and non carcinogenic risk was calculated from the ADD.

4.1. Average Daily Dose

ADD values ranged as follows; (Li) 5.59×10^{-6} to 3.8×10^{-4} , (V) 1.12×10^{-6} to 1.9×10^{-5} , (Cr) 1.86×10^{-6} to 4.49×10^{-5} , (Mn) 3.1×10^{-4} to 4×10^{-3} , (Fe) 2.9×10^{-3} to 0.2, (Co) 7.6×10^{-6} to 1.3×10^{-4} , (Ni) 1×10^{-5} to 4.4×10^{-4} , (Cu) 5.2×10^{-5} to 3.1×10^{-3} , (Zn) 1.7×10^{-4} to 9.4×10^{-2} , (As) 4.6×10^{-7} to 5.4×10^{-4} , (Sr) 2.2×10^{-4} to 2.3×10^{-2} , (Cd) 2.7×10^{-7} to 3.1×10^{-5} , (Ba) 5.6×10^{-5} to 2.6×10^{-3} , (Pb) 6.8×10^{-6} to 1.3×10^{-4} as in **Figure 10**.

4.2. Hazard Quotient

HQ values ranged as follow; 5.6×10^{-4} to 9.5×10^{-3} (V), 1.2×10^{-3} to 7.7×10^{-2} (Cu), 1.9×10^{-3} to 3.8×10^{-2} (Pb), 5.7×10^{-4} to 3.1×10^{-1} (Zn), 4.1×10^{-3} to 2.9×10^{-1} (Fe), 2.1×10^{-2} to 2.9×10^{-1} (Mn) as in **Figure 11**.

4.3. Carcinogenic Risk

CR for the carcinogenic elements; Pb, Cr, Cd, Ni and As are; 9.4×10^{-6} to 1.1×10^{-2} (As), 2.1×10^{-6} to 2.5×10^{-4} (Cd), 1.0×10^{-4} to 2.5×10^{-4} (Cr), 1.2×10^{-5} to 4.9×10^{-4} (Ni) as in **Figure 12**.

Table 7. Parameters used for estimating exposure assessment (Lushenko, 2010).

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

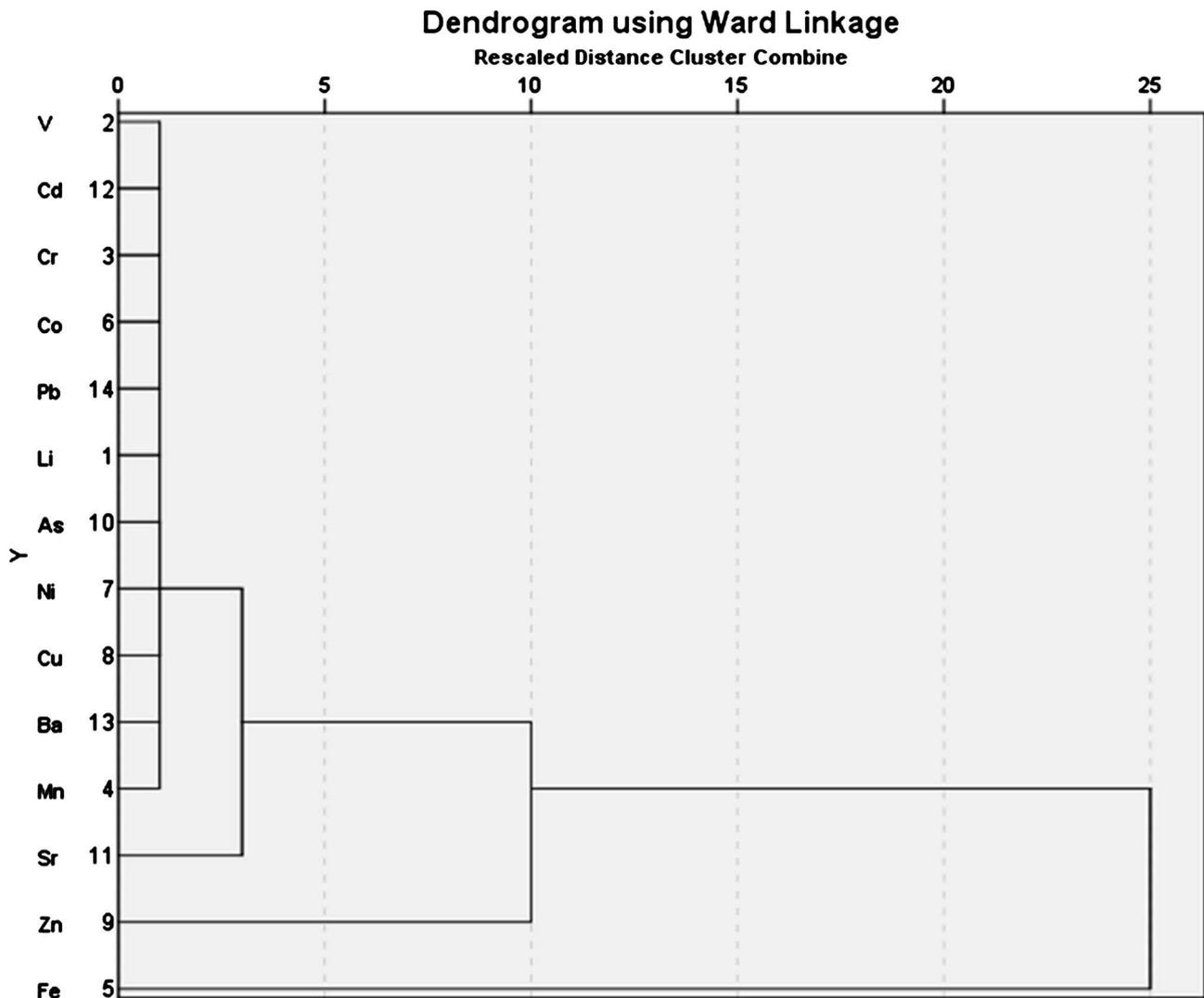


Figure 9. Dendrogram of trace metals in groundwater of the Akwa-Mundemba area made up of two clusters: Cluster one (1) Fe, soluble. Cluster (2), slightly soluble is divided into two classes; class (1) Zn, immobile. Class (2) further divided into two subclasses; subclass (1) Sr, slightly mobile. Subclass two V, Cd, Cr, Co, Pb, Li, As, Ni, Cu, Ba and Mn; mobile under present EC, pH and temperature conditions: Probably from different parent rocks.

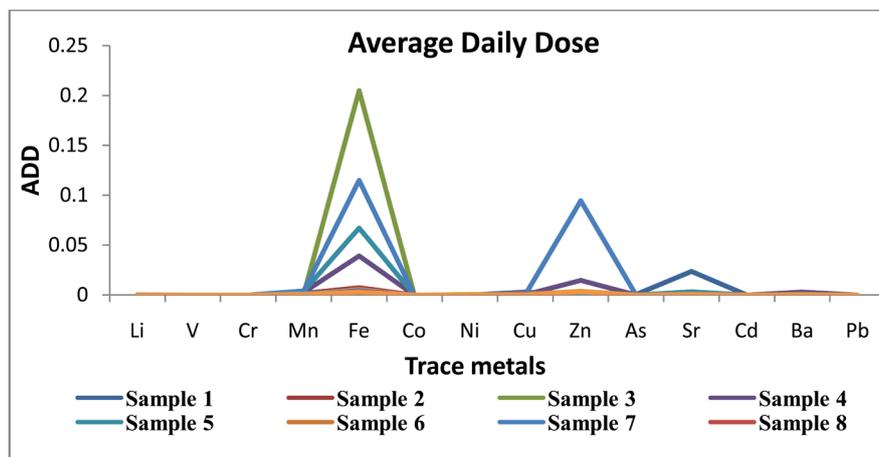


Figure 10. Average daily dose (ADD) of trace metals through water intake. All values are below toxic level.

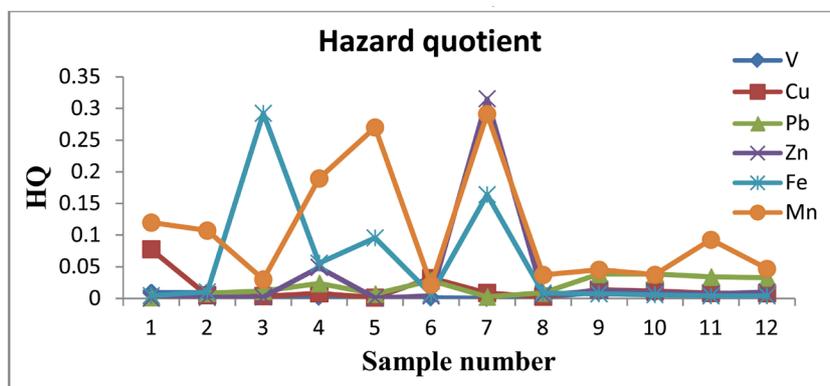


Figure 11. Hazard quotient (HQ) of trace metals through water intake. The values of Iron in sample 3, Manganese in sample 5, and Vanadium & Copper in sample 7 are relatively high but all values are below toxic levels.

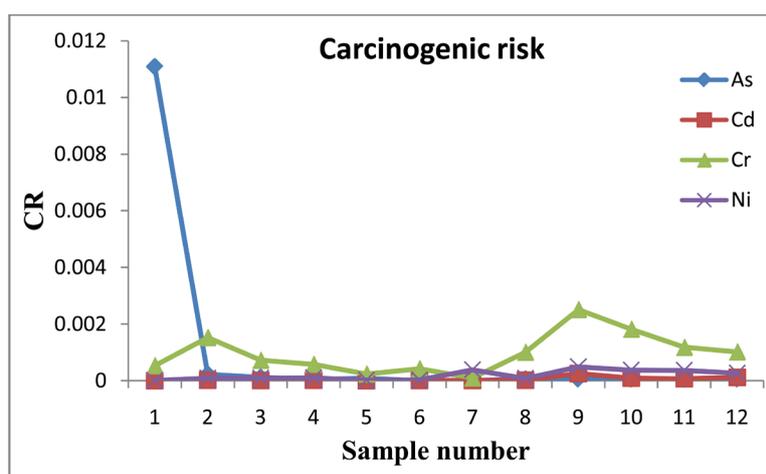


Figure 12. Carcinogenic risk (CR) of each contaminant. The values in sample 1 (Idabato II) is relatively high. All values are below toxic levels.

4.4. Hazard Index

HI is the cumulative sum of HQ. The values ranged between 0.06 and 0.78 for each of contaminant indicating no toxicity as in **Figure 13**.

All the groundwater risk indices; ADD, CR, HQ and HI were less than 1 in categories of insignificant health risk as shown in **Table 8**.

5. Pollution Evaluation Indices

5.1. 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 -13.5 to -11 as shown in **Figure 14**. According to the classification of **Edet and Offiong (2002)**, 100% of the samples have low degree of contamination factors.

5.2. Enrichment Factor

Iron (Fe) was chosen as a stationary reference element to perform this calcula-

tion (Agunbiade et al., 2009). 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 (Liaghati et al., 2003). The enrichment factors of heavy metals in Mundemba were as shown in Figure 15 and Table 9. The sequence of EF in the sediments was As > Pb > Ba > Zn > Co > Cd > Ni > Mn > Sr > Zn > Li > Cu > Cr > V. EF values in the study area are between 0.26 to 35.47 which is indicative of significant enrichment and that the source of these metals is from natural and anthropogenic processes. Arsenic is the most enriched element in the study area; this could be attributed to agricultural wastes.

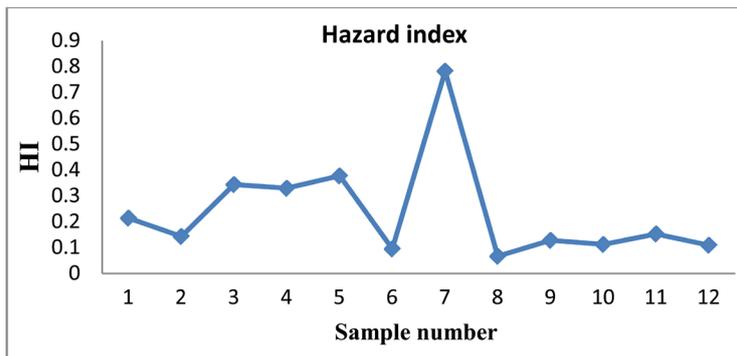


Figure 13. Non carcinogenic toxic risk index or hazard index (HI) of trace metals through water intake. The values in sample 7 (Isangele) is relatively high. All values are below toxic levels.

Table 8. Summary classification of health risk assessment carcinogenic and non-carcinogenic risk in Akwa-Mudemba.

Index	Range	Classification	Samples	(%)
CR	greater than 10E-6 and less than 10E-4	Generally satisfactory	10	83.3
	>10 ⁻⁴	Intolerable	2	16.7
HQ	<1	Acceptable level (no concern)	12	100
	>1	No carcinogenic adverse effects	-	-
HI	<1	Safe	12	100
	>1	Unsafe	-	-

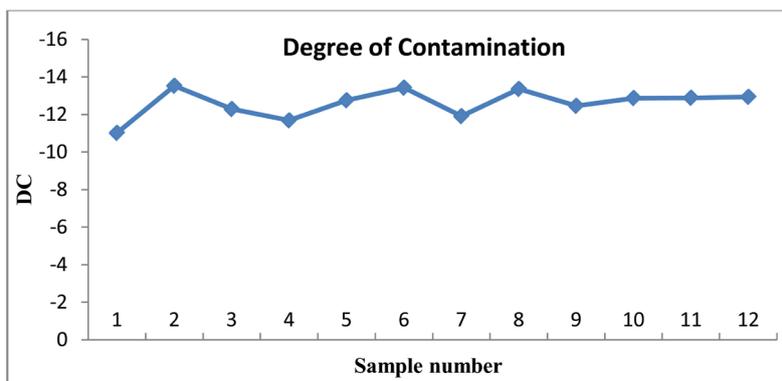


Figure 14. The degree of contamination for trace metals of groundwater in Mudemba.

5.3. Ecological Risk Assessment

5.3.1. 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 -29.92 to -0.39 ($Er < 40$). RI of the studied trace metals

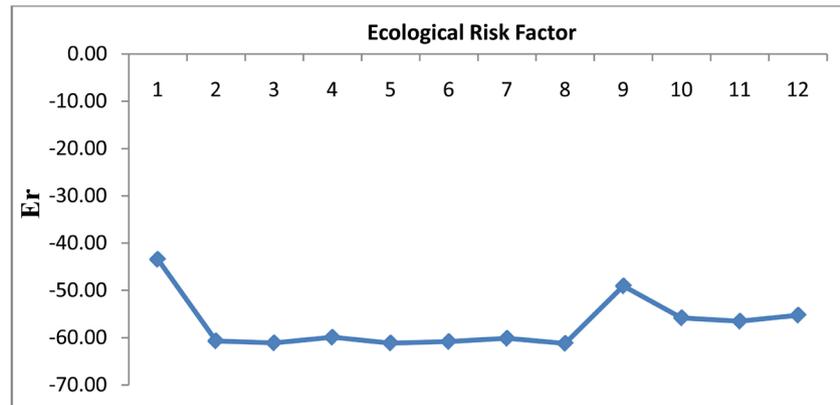


Figure 15. The enrichment factor for trace metal of groundwater in Mudemba. Cobalt, Arsenic and Lead are being enriched.

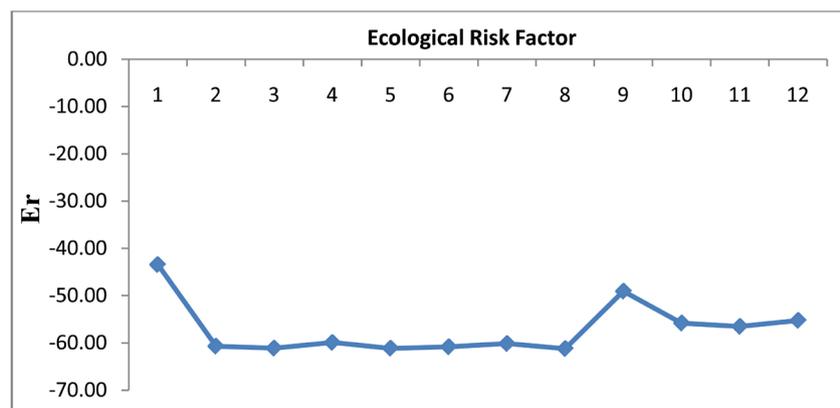


Figure 16. The ecological risk factor Er for trace metal of groundwater in Mudemba.

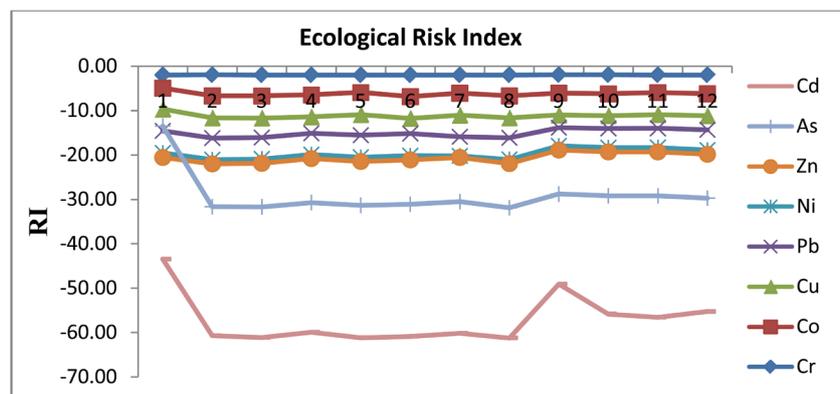


Figure 17. The ecological risk index for trace metal of groundwater in Mudemba.

Table 9. The Geo-accumulation index (Igeo) of Mundemba groundwater.

SN	Li	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Sr	Cd	Ba	Pb
1	4.8E-4	2.3E-05	3E-06	5.3E-3	3.9E-2	8.2E-06	4.5E-05	3.9E-2	5.4E-3	3.4E-05	0.6	4.8E-09	4E-4	3.E-06
2	2.6E-05	2.4E-05	9E-06	4.8E-3	9.1E-2	1.1E-06	3.5E-4	2.5E-3	2.E-2	7.2E-07	0.02	5.8E-08	2E-05	1.3E-05
3	2.8E-05	7.6E-06	4E-06	1.3E-3	2.6	1.E-06	3.4E-4	1.9E-3	0.02	3.8E-07	0.01	3.5E-08	9E-05	1.8E-05
4	7.7E-05	5.8E-06	3E-06	8.4E-3	0.4	2.1E-06	3.8E-4	4.2E-3	0.4	1.6E-07	0.06	4.9E-08	1.3E-3	3.7E-05
5	8E-05	4.2E-06	1E-06	1.2E-2	0.8	4.2E-06	9.7E-05	7E-4	7.7E-3	2.9E-07	0.08	1.1E-08	2E-4	1.1E-05
6	8E-05	2.8E-06	2E-06	1E-2	6.2E-2	4.8E-07	1.1E-4	1.6E-2	0.04	2.9E-08	0.01	1.8E-08	1E-4	4.4E-05
7	7.1E-05	1.4E-06	6E-07	1.3E-2	1.4	3.6E-06	1.46E-2	4.4E-3	3.0	6.7E-08	0.01	2.4E-08	9E-05	4.4E-06
8	3.2E-05	6.6E-06	6E-06	1.7E-3	7.6E-2	1.2E-06	3.1E-4	1.4E-3	0.05	2.1E-07	0.01	4E-08	3E-4	1.4E-05
9	5.3E-05	2.3E-05	1E-05	2E-3	6.6E-2	3.5E-06	1.8E-3	7.1E-3	0.12	1.8E-07	0.01	5.8E-07	2E-4	6.E-05
10	7.3E-05	2.1E-05	1E-05	1.7E-3	5.5E-2	2.9E-06	1.4E-3	6E-3	0.08	1.8E-07	0.01	2E-07	1E-4	6.E-05
11	7.1E-06	1.5E-05	7E-06	4.1E-3	3.7E-2	4.1E-06	1.3E-3	4.2E-3	0.06	1.8E-07	0.02	1.6E-07	1E-4	5.3E-05
12	5.9E-05	1.6E-05	6E-06	2.1E-3	3.7E-2	3E-06	1E-3	4.1E-3	0.1	1.8E-07	0.01	2.7E-07	2E-4	5.1E-05
min	7.1E-06	1.4E-06	6E-07	1E-3	3.7E-2	4.8E-07	4.5E-05	7E-4	5.4E-3	2.9E-08	0.01	4.8E-09	2E-05	3.E-06
max	4.8E-4	2.4E-05	1E-05	1.3E-2	2.6	8.2E-06	1.85E-3	3.9E-2	3.0	3.4E-05	0.6	5.8E-07	1.3E-3	6.E-05
mean	8.9E-05	1.2E-05	6E-06	4.8E-3	0.4	3E-06	7.3E-4	7.7E-3	0.3	3.0E-06	0.07	1.2E-07	3E-4	3.E-05

ranged from -61.2 to 43.42. All the samples show low ecological risk index, this indicates low polluted according to (Hakanson, 1980).

5.3.2. Pollution Load Index (PLI)

This index is a quick tool in order to compare the pollution status of different places (Adebowale et al., 2009). The values of Pollution Load Index are <1 which is indicative that there is no pollution as shown in Figure 18. These results attributed principally to natural sources.

5.3.3. Geo-Accumulation Index Igeo

Geo-accumulation index Igeo, is a quantitative measure of the degree of pollution in groundwater as shown in Table 9 presents the indices for the quantification of trace metal accumulation in the Akwa-Mudemba (Singh et al., 1997). The values range as in Table 4. Groundwater is unpolluted to strongly polluted by Fe in samples 3, 5 & 7 and Zn in samples 3, 4 & 7; while it is unpolluted to moderately polluted by Sr in all 12 samples. The other eleven trace metals are not polluting the groundwater in Akwa-Mudemba area.

The summary of results for the evaluation of pollution indices is presented in Table 10.

The mostly neutral pH, low temperatures, low TDS, low EC and the short residence time of ground water due to high gradients; are conditions unfavourable for trace metal oxidation and dissolution in groundwater. This implies that conditions are unfavourable for the accumulation of the trace metals in the fluid phase. A reason for the absence of high concentrations of trace metals in groundwater of

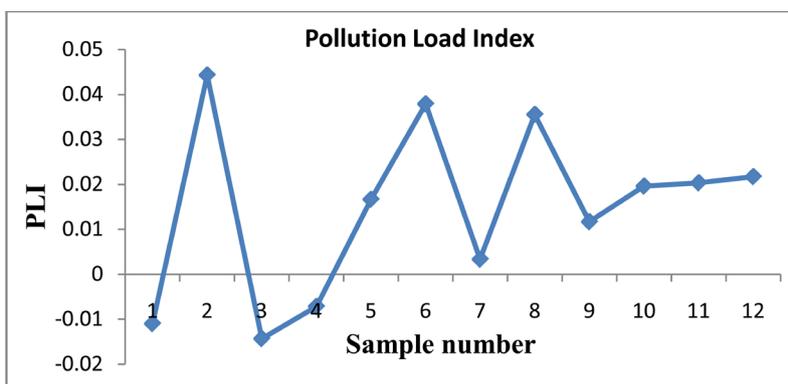


Figure 18. The pollution load index for trace metal of groundwater in Mudemba.

Table 10. Summary Classification of Akwa-Mudemba groundwater based on pollution evaluation indices.

Index	Range	Classification	SN	%
DC	<10	Low degree of contamination factor	12	100
	≤1	Background contamination	4	33.4
	1 - 2	Minimal enrichment	1	8.3
EF	2 - 5	Moderate enrichment	1	8.3
	5 - 20	Significant enrichment	5	41.7
	20 - 40	Very high enrichment	1	8.3
Er	<40	Low potential risk	12	100
RI	<150	Low ecological risk	12	100
PLI	<1	No pollution	12	100
	≤0	No-pollution	Pb, Co, Cu, Cr, Mn, Sr, Cd, V, Ni, As, Li, Ba, Mn	
Igeo	0 - 1	No pollution to moderately pollution	Sr, Fe, Zn	
	1 - 2	Moderately pollution to pollution	Fe, Zn	
	2 - 3	Pollution to strong pollution	Fe, Zn	

Akwa-Mudemba though they may be present in the parent rock and soil.

The concentrations of trace metals in groundwater have also been reported below guidelines in Shanghai, China (Xu et al., 2004); Tuscany, Italy (Tamasi & Cini, 2004); and USA (Thomas et al., 1998).

6. Conclusion

The groundwater in the Akwa-Mudemba area 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 trace metals but trace metals are being enriched. Thus, from health risk indices and pollution evaluation indices of trace metals, the groundwater in Akwa-Mudemba area is safe for drinking.

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

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

The high iron concentrations could be attributed to the presence of rocks containing high concentrations of magnetite and hematite.

Conflicts of Interest

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

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