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TRACE METAL ASSESSMENT OF GROUNDWATER IN THE COASTAL AQUIFEROUS FORMATIONS OF LIMBE, FAKO DIVISION, SOUTHWEST REGION, CAMEROON

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ABSTRACT

Groundwater is known to be an important resource in Cameroon and the population of Limbe in particular relies on such a resource. Located along the coastal area and headquarters of the Fako Division in the Southwest Region of Cameroon, Limbe is a cosmopolitan city, situated between 3.96-4.06N and 9.15-9.24E. Due to the carcinogenic and non-biodegradable nature of trace metals, aquifers are contaminated with their presence, making water from these sources unsafe for consumption. The aim of this study was to assess the concentration of trace metals in groundwater and compare them with WHO limits. Materials used in this study were GPS receiver, EC meter, pH meter thermometer, filters, permanent marker, diluted nitric acid, sampling containers, Golden Surfer Software, Global Mapper, IBM SPSS. Methodology adopted in the study included fieldwork and sampling, pre-laboratory preparation, index calculation and data synthesis. 175 hand-dug wells, 10 boreholes, streams and rivers were sampled in this study. Ten groundwater samples were collected from six pre-selected hand-dug wells, two boreholes, a stream and a spring for trace metal analysis using ICP-MS analytical technique. The results showed that all the trace metals were averagely below permissible limits with Zn being the highest recording 465µg/L at Motowoh-New Town and Cd the lowest in concentration. Trace metal concentration was in the order of Zn > Sr > Mn> Ba > Fe > V > Cu > Cr > Ni > Co > Pb > As > Li > Cd. An anomalous concentration of Ba with 83µg/L was recorded at Half Mile. Health risk assessment was done on the basis of Average Daily Dose (ADD) with values ranging between 1.3×10^{-6} and 1.5×10^{-2} mg/kg/day, Carcinogenic Risk (CR) between 1.6×10^{-5} 0.00704, Hazard Quotient (HQ) between 0.0027 and 0.5657, Hazard Index (HI) between 0.0171 and 0.5826. Pollution risk indices were calculated following Degree of Contamination (DC) with values ranging between 0.66 and 2.92, Enrichment Factor (EF) between 0.002 and 2.84, Ecological Risk Assessment with ecological risk factor ranging between 0.00292 and 1.7 and ecological risk index between 1.707 and 4.23, Pollution Load Index (PLI) varied between 0.014 and 0.037 and Geo-accumulation Index (Igeo) all less than zero. Generally, groundwater in Limbe and environs was found unpolluted. Health risk indices showed that groundwater was generally satisfactory, safe for consumption and pose no carcinogenic risk. All metals except Zn were from natural processes. Zn was the most enriched trace metal.

Keywords: Trace Metal, Assessment, Groundwater, Aquiferous Formations, Limbe-Cameroon

1. INTRODUCTION

Trace metals are released into the environment either by geogenic processes such as rock weathering and volcanic activities or by anthropogenic processes such as mining, agriculture and industrial manufacturing. Trace metals pose serious threats to human health and the environment because of their non-biodegradable nature and aquiferous formations contaminated with these metals are unsafe for consumption because they can potentially enhance the risk of cancer in humans [1] and a wide range of other human health problems such as hypertension, vascular disease, and lung disease [2] and are suspected of causing birth defects and reproductive disorders [3]. Water is a unique resource, without which life is impossible [4] and its importance cannot be overemphasized. Trace metals are a group of chemical components that occur in natural systems at low concentrations, in mass fractions of parts per million or less and are toxic to living organisms [5].

Groundwater contamination with trace metals is one of the most important environmental issues in the world [6], especially as a high proportion of the world's population is turning towards groundwater. Rapid urbanization, agricultural activities, and natural geochemical processes are affecting directly or indirectly on the chemical composition of groundwater day by day [7], where we have metals that occur in traces in water. Some of these trace metals include; 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 [8].

Groundwater contamination with trace metals is usually controlled by the geochemical heterogeneity of the aquifer and/or anthropogenic activities on land. In an area rich in water resources and where the population is growing very rapidly like the Mount Cameroon area, it is very important to assess the water quality [9]. Groundwater is known to be the most important resource in Cameroon [10] and the population of Limbe in particular relies on such a resource. Trace metals assessments have been carried out in soil along the lower slopes of Mount Cameroon area for their potential toxicity to humans and the ecosystem [11], in Bamenda [12] Studies on the spatial distribution of trace metals in groundwater can help to better comprehend their varying sources and scrutinize the extents of contamination. The aim of this study was to assess the concentration of trace metals in groundwater and compare them with WHO limits. With the population explosion and the increased need for groundwater, understanding the existing situation of the aquiferous formations in Limbe is of utmost importance for human health and environmental sustainability. It is against this background that this research was carried out in two seasons.

2. STUDY AREA

Located along the coastal area and headquarters of the Fako Division in the Southwest Region of Cameroon, Limbe is a cosmopolitan city, situated between 3.96-4.06N and 9.15-9.24E **(Figure 1)**. The indigenous people include the Bakweri, Isubu, and Creoles [13], with a surface area of 5km^2 and a population currently estimated at over 130,000 inhabitants [14], with most of them being low income earners. Economic activities in this area include farming, fishing, and petty trading [15]. Limbe is one of the major petroleum and agricultural cities in the country, with beautiful coastal beaches, historic monuments, a botanic garden, and a wildlife center [16]. These encourage for the high migration of many people who benefit on the natural resources of the city.

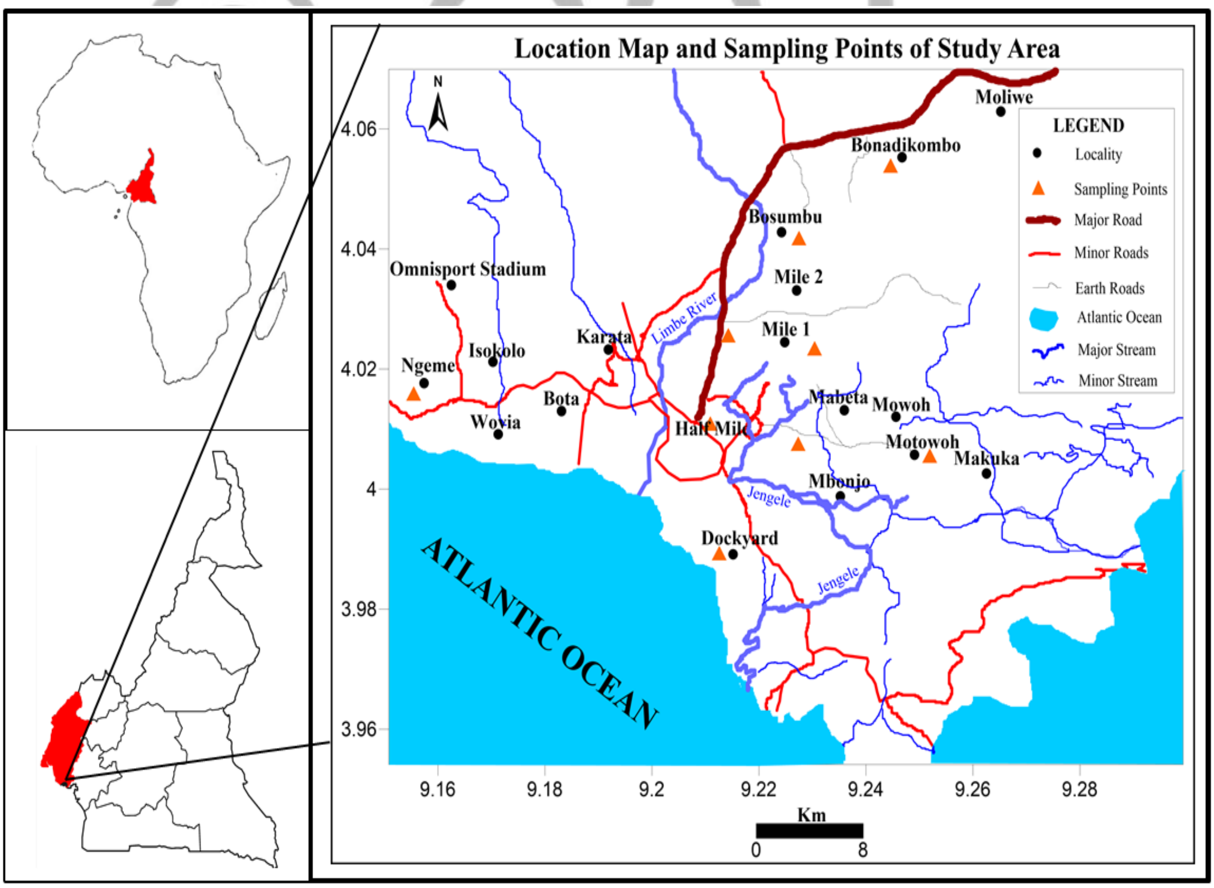

Figure 1: Location Map and Sampling Sites of the Study Area

2.1 Drainage

Limbe and Jengele are the two main rivers in the study area with the former being the largest. River Limbe takes its rise from Mt Cameroon, through Mile 4, Mile 2, Middle Farms, Botanic Garden and into the Atlantic Ocean. River Limbe has a trellis drainage pattern with all its numerous tributaries running parallel down the slopes of Mount Cameroon. The slopes are steep, up to 43%, causing the streams to flow with high velocities [17]. Other smaller streams include Mange, Sange Mile 4, Grand Lake-Mile 2, Konkikar, Balimba-Mabeta New layout, Motowoh water and Ndiba water. There are numerous springs notably: Likomba, Toma-Mile 4, Busumbu spring-Mile 2, Cold source Mile 1 and Crystal garden. Gravity catchments have been constructed around some other smaller springs for additional water supply; Mile 4, Mabeta, Mowoh, Motowoh, Batoke. The rivers empty into the Atlantic Ocean.

2.2 Hydrogeological Setting

Little work has been done on the hydrogeology of Limbe with sparse data to correlate. As reported by [17], some groundwater baseline hydrogeochemical studies have been carried out around Mount Cameroon [9] [18] [19] [20]. Just recently, a characterization of groundwater in the basaltic fractured rock aquiferous formations of Limbe [17] was carried out.

The Limbe area is made up mostly pyroclastic and of jointed weathered fractured and columnar basalt resulting in volcanic fractured rock aquifers where saturated. Limbe, being a coastal area experiences rise and fall in seawater levels. This powerfully controls the amount of solutes that leaves or enters the aquifer in a process of seawater intrusion.

2.3 Geological Setting

Limbe is a geohazard zone in the southwest region with past history of numerous volcanic activities, landslides and floods [21] [22] [23] [24]. Limbe rests on the slopes of Mount Cameroon and forms part of the Cameroon Volcanic Line. It is between the Rio del Rey and Douala basins. As a result of volcanic eruptions of Mount Cameroon, the main rock types in this area include basalt, basanites, lahar deposits and pyroclastic materials **(Figure 2)**, exposed at the surface or are covered by extremely fertile dark brown, reddish brown, yellowish and/or pale yellow sticky, clay, silt and silty clayey soils [25]. The geology is of tertiary basaltic rocks composed of multiple porphyritic basaltic lava flows. The mineral content of basalts in Limbe consists mainly of Clinopyroxene, Hematite, and Goethite and the soils comprises mainly of Anatase, Annite, Augite, Goethite, Hematite, and Kaolinitic.

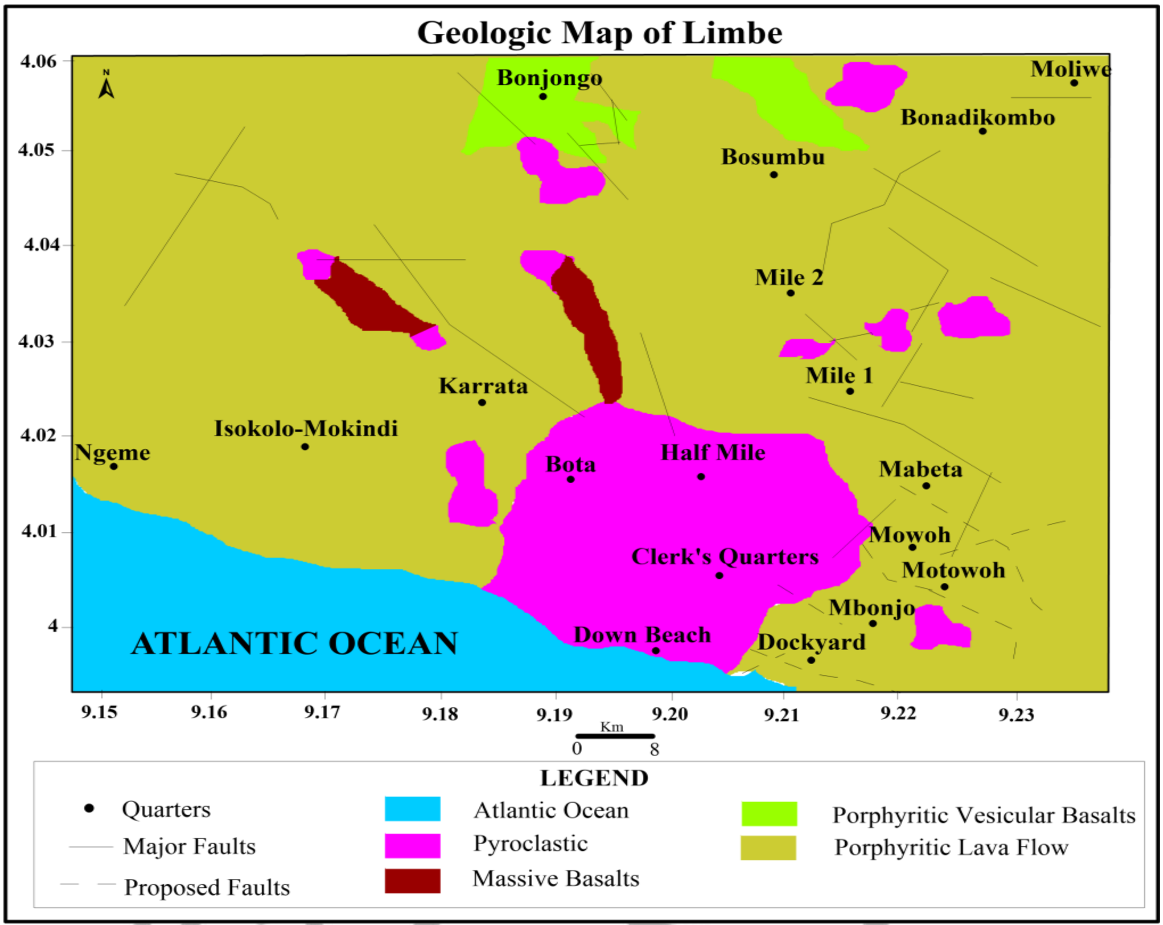

Figure 2: Geologic Map of Limbe (Modified from [17])

3. MATERIALS AND METHODS

Different materials and methods necessary for the completion of this study were used. Various methods used to calculate pollution and health risk indices associated with trace metals in groundwater were all sought.

3.1 Materials

Table 1: Materials used, their identities and respective functions

Material	Identity	Functions
	FIEDWORK	
GPS	GARMIN GPSMAP 60CSx	To measure longitude, latitude and elevation of wells, streams and springs
EC Meter	HANNA HI 98304/ HI98303	To measure Electrical Conductivity of water
pH Meter	HANNA HI 98127/ HI98107	To measure water pH
Thermometer	Extech 39240 (-50°C to 200°C)	To measure water temperature
	DATA SYNTHESIS	
Golden SurferSoftware	Version 12	GIS plotting contours for spatial distribution

Global Mapper	Version 11	Geolocation of wells, boreholes and streams
IBM SPSS	Version 25	For statistical operations
Microsoft Excel	Version 2010	For statistical operations
	LAB PREPATION	
Filters	0.2µm cellulose based ester syringe filter in a polystyrene case (Advantech AS020AN)	To filter water samples by removing suspended solids for preservation
Cellulose Tape	Adhesive masking seal	For sealing of sample bottle
Permanent Marker	Black and blue inked marker	For labelling of the containers prior to posting
Diluted Nitric Acid	Drops of 2ml	Water sample preservation
Sampling Containers	Polystyrene 500ml	For storing and preserving water samples for onward transmission to laboratory

3.2 Methodology

Methods adopted in this study were divided into three classes; fieldwork and sampling methods, pre-laboratory preparation method and index calculation and data synthesis method.

3.2.1 Fieldwork and Sampling Method

175 hand-dug wells, 10 boreholes, streams and rivers were sampled in this study. During this field traverse, a GPS was used to get readings of the coordinates at each location and camera used to take photographs of wells.

During sampling, small quantity of water was carried in case of streams, springs and boreholes or pulled out using a bucket in case of a well and the tip of the Triameter was immediately inserted into the water, and readings for temperature, EC, and pH were obtained simultaneously. In wells, the well depths and static water levels were gotten using a 100m measuring ribbon tape and collar heights, diameters of wells using a 5m measuring steel tape. Distance from the well to available dumpsites around, pit toilets and/or sewage tanks were all measure and the presence or absence of a well cover on each well was noted.

3.2.2 Pre-Laboratory Preparation Method

Ten groundwater samples were collected from six pre-selected hand-dug wells, two boreholes, a stream and a spring for trace metals analysis. Prior to sample collection, the sampling bottles were thoroughly rinsed with the water to be sampled so as to avoid contamination. The samples in 50ml were acidified and sent to the Activation Laboratory in Ontario, Canada in December 2019 for analysis using ICP-MS analytical technique, and the results were sent by mail after 6 weeks

3.2.3 Index Calculation and Data Synthesis Method

This method gives an account of how the indices were calculated and the results obtained. It makes use of various equations, formulae and software usage for the production of location and spatial images.

Hazard Identification

This is the process of determining whether exposure to a stressor can cause an increase in the incidence of specific adverse health effects likely to occur in humans and what health effects are caused by the pollutants. It also involves the characterization of potential contaminants and their relative mobilities [26].

Dose-Response/Toxicity Assessment

This is a relationship that quantitatively evaluates human health risk associated with the chemical of concern in the study area. The shape of the dose-response relationship depends on the agent, the kind of response, and the experimental subject [27]. In this step, the Reference Dose (RfD) will be used for non carcinogenic risk.

Exposure Assessment

This process estimates the magnitude, frequency, and duration of human exposure to an agent in the environment, or estimates future exposures for an agent that has not yet been released [27]. The main exposure pathway taken into consideration in this study was intake of the metals through water consumption. The intake of metals through ingestion of groundwater was calculated using the following equation [28]

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

Where, ADD is Average Daily Dose (mg/kg/day); C is Concentration of contaminant in the environmental media (e.g. µg/L, mg/L); IR is Ingestion rate per unit time (mg/day or L/day); EF is Exposure frequency (days/years); 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 **(Table 2)**

Table 2: Parameters to Characterize the ADD Values [29]

Exposure parameters	Symbols	Units	Value
Concentration of Trace metals	C	mg/L	
Ingestion rate	IR	L/day	2.2
Exposure frequency	EF	Days/year	365
Exposure duration	ED	Years	70
Body weight	BW	Kg	70
Average time	AT	Years	25,550 days

Risk Characterization

The health risk was assessed in relation to its non-carcinogenic as well as carcinogenic effects based on the calculation of ADD estimates and defined toxicity according to the following relationship [30]

Carcinogenic Risks: For carcinogenicity, the probability of an individual developing cancer over a lifetime was estimated by multiplying the cancer slope factor (SF) in mg/kg/day for the substance by the chronic or average daily dose (ADD) daily intake (mg/kg/day), whose result is unit less. The cancer risk for individulas was calculated using the following equation [27]

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

SF is the slope factor of the contaminant mg/kg/day. 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 [31]

Non Carcinogenic Risks: To estimate non carcinogenic risk in this study, the following equation [27] was used for the calculations.

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

Where HQ = Hazard Quotient, ADD = Average Daily Dose and RfD = Reference Dose

Table 3: The Toxicity Responses to Trace Metals as the oral reference dose [30]

Heavy metals	**Oral R_fD (mg/kg/day)**
Cd	5.0×10^{-4}
Cu	0.04
Pb	3.5×10^{-3}
Zn	0.3
Fe	0.7
Mn	0.014

If the calculate HQ is less than 1, then no adverse health effects are expected. If HQ is greater than 1, then adverse health effects are possible [32]. If the level of a given metal is higher than RfD, then it may have harmful effects on human health [33]. The Hazard Index (HI) is the sum of the HQ values for different metals. It is given by the following formula;

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

Pollution Risk Indices

In this study, trace metal pollution indices that were investigated included; Degree of contamination (Cd), Enrichment factor (EF), Ecological risk factor (Er), Ecological risk index (RI), Pollution load index (PLI), and Geo-accumulation index (Igeo) .

Degree of Contamination [34], $DC = \sum_{i=1}^{n} C_f^i$ ....(5)

Enrichment factor [35], $EF = \frac{(Ci/Cie)sample}{(Ci/Cie)background}$ ....(6)

Ecological risk factor [36], $E_r^i = T_r^i x C_r^i$ ....(7)

Ecological risk index [36], $RI = \sum_{i=1}^{n} E_r^i$ ....(8)

Pollution load index [37], $PLI = \sqrt[n]{C_{f1} x C_{f2} .... C_{fn}}$ ....(9)

Geo-accumulation index [38], $I_{geo} = \log_2 [C_i / (1.5 C_{ri})]$ ....(10)

Software Usage

IBM Statistical Package for Social Sciences (SPSS) version 25.0 and Excel-statistical software were used to give spatial variations of trace metals using multivariate analysis. Microsoft Excel was used on numerical data to generate, calculate and statistically analyze the mean, maximum and minimum values of metals concentrations and their coefficients of variation.
Golden Surfer software, Version 12 was used for GIS plotting of spatial distribution maps. Global Mapper Software version 11.0 was used to assess spatial continuity of data and realization of standard maps for easily interpretation of data, analyses, procession of data, and providing support for virtually every known spatial file format as well as direct access to common spatial databases.

4. RESULTS AND DISCUSSION

4.1 In-situ Physicochemical and Physical Parameters

The measured physicochemical parameters of groundwater in the study area were temperature (Temp), pH, Electrical Conductivity (EC) and Total Dissolved Solid (TDS) and physical parameters were elevation, Depth-to-Static Water Level (DSWL) and groundwater flow direction. These parameters showed great seasonal variations, indicating that the aquiferous formations were influenced by seasonal changes.

Table 4: DSWL and In-situ Physicochemical Parameters in Accordance with Standards Values for Drinking Water [39]

	Wet Season			Dry Season			WHO
Parameters	**Max**	**Min**	**Mean**	**Max**	**Min**	**Mean**	**limit [39]**
Temp (°C)	29.1	22	26.81	32.5	23.5	28.48	0 – 30
pH	9	6.2	7.97	6.4	5.16	5.73	6.5 - 8.5
EC (µS/cm)	1367	73	277.16	1222	68	303.05	750
TDS (mg/L)	764.47	49.58	187.75	818.74	45.56	203.04	500
DSWL	17.8	0.17	1.85	21.6	0.25	2.48	

4.2 Trace Metal Assessment

The results for ten groundwater samples collected in Limbe showed that all the trace metals were averagely below permissible limits [39] with Zn being the highest and Cd the lowest. An anomalous concentration of Ba with 83µg/L was recorded at Half Mile in Sample 5. Zn showed highest concentration with a maximum value of 465µg/L recorded at Motowoh-New Town **(Table 5)**.

Table 5: Trace Metal Concentration (µg/L) and Basic Statistics for Groundwater

Sample ID	Li	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Sr	Cd	Ba	Pb
S_1 (Borehole) – Ngeme	0.6	14.7	0.7	1.5	10	1.3	0.9	3.4	217	0.13	136	0.1	11	1.2
S_2 (Borehole) – New Town	0.7	21.7	4	2.1	30	1.5	1.5	3.4	257	0.11	102	0.1	8.4	1.3
S_3 (Well) – Dockyard	0.3	9.1	0.4	0.7	10	0.3	1.7	4.8	15.4	1.34	296	0.1	19	0.9
S_4 (Well) – Motowoh	0.5	0.8	1.5	2.7	20	2.6	2.7	3.8	465	0.13	105	0.2	69	1.5
S_5 (Well) – New Market	0.9	1.5	0.9	252	60	0.8	1.8	2.3	21.4	0.23	307	0.1	**83**	1.1
S_6 (Well) – Alpha Club	0.3	5.5	0.8	0.9	20	0.3	1.1	1.8	20.7	0.1	165	0.1	38	0.9
S_7 (Well) – Espoir Road	0.4	1.5	0.4	1.7	10	0.6	0.9	1.3	56.1	0.04	161	0.1	31	1.1
S_8 (Well) – Bonadikombo	0.1	2.5	1.6	1.5	40	0.8	1.3	1.6	95.1	0.06	152	0.1	42	0.8
S_9 (Stream) – Bonadikombo	0.6	1.4	0.6	1.2	20	0.6	0.8	2	79.4	0.07	206	0.1	21	1.3
S_{10} (Spring) – Bosumbu	0.5	17	0.9	0.6	10	0.3	0.9	1.4	14.6	0.18	130	0.1	3.1	0.8
Maximum	**0.9**	**21.7**	**4**	**252**	**60**	**2.6**	**2.7**	**4.8**	**465**	**1.34**	**307**	**0.2**	**83**	**1.5**
Minimum	**0.1**	**0.8**	**0.4**	**0.6**	**10**	**0.3**	**0.8**	**1.3**	**14.6**	**0.04**	**102**	**0.1**	**3.1**	**0.8**
Mean	**0.49**	**7.57**	**1.18**	**26**	**23**	**0.9**	**1.36**	**2.58**	**124.2**	**0.24**	**176**	**0.1**	**33**	**1.1**
WHO Limit	**200**	**200**	**50**	**400**	**2000**	**10**	**70**	**2000**	**5000**	**10**	**400**	**3**	**70**	**10**

The high concentration of Ba in the well at New Market (S5) could be as a result of the presence of a barium mineral in the surrounding or underlying rocks. A mineral like barite that occurs in marine deposits or sedimentary rock such as limestone or romanechite (in association with manganese) or harmotome that occurs with calcite in the amygdaloidal cavities of volcanic rocks is a suggestive indicator for Ba in this part of the study area.

4.2.1 Health Risk Assessment

Average Daily Dose (ADD)

The ADD values ranged between 1.3 x 10^{-6} and 1.5 x 10^{-2} mg/kg/day and were all below harmful levels. Zn had the highest value and Cr the lowest value **(Table 6)**. Daily intake in Limbe, was the order of Zn > Sr > Mn> Ba > Fe > V > Cu > Cr > Ni > Co > Pb > As > Li > Cd **(Figure 3)**.

Table 6: Calculated Maximum, Minimum and Mean Values for Average Daily Dose

Element	Maximum	Minimum	Mean
Li	2.8×10^{-5}	3.1×10^{-6}	1.5×10^{-5}
V	6.8×10^{-4}	2.5×10^{-5}	2.4×10^{-4}
Cr	1.3×10^{-4}	1.3×10^{-5}	3.7×10^{-5}
Mn	7.9×10^{-3}	1.9×10^{-5}	8.3×10^{-4}
Fe	1.9×10^{-3}	3.1×10^{-4}	7.2×10^{-4}
Co	8×10^{-5}	8.2×10^{-6}	2.8×10^{-5}
Ni	8.5×10^{-5}	2.5×10^{-5}	4.3×10^{-5}
Cu	1.5×10^{-4}	4.1×10^{-5}	8.1×10^{-5}
Zn	1.5×10^{-2}	4.6×10^{-4}	3.9×10^{-3}
As	4.2×10^{-5}	1.3×10^{-6}	7.5×10^{-6}
Sr	9.6×10^{-3}	3.2×10^{-3}	5.5×10^{-3}
Cd	5.3×10^{-6}	1.9×10^{-6}	3.3×10^{-6}
Ba	2.6×10^{-3}	9.7×10^{-5}	1×10^{-3}
Pb	4.8×10^{-5}	2.6×10^{-5}	3.4×10^{-5}

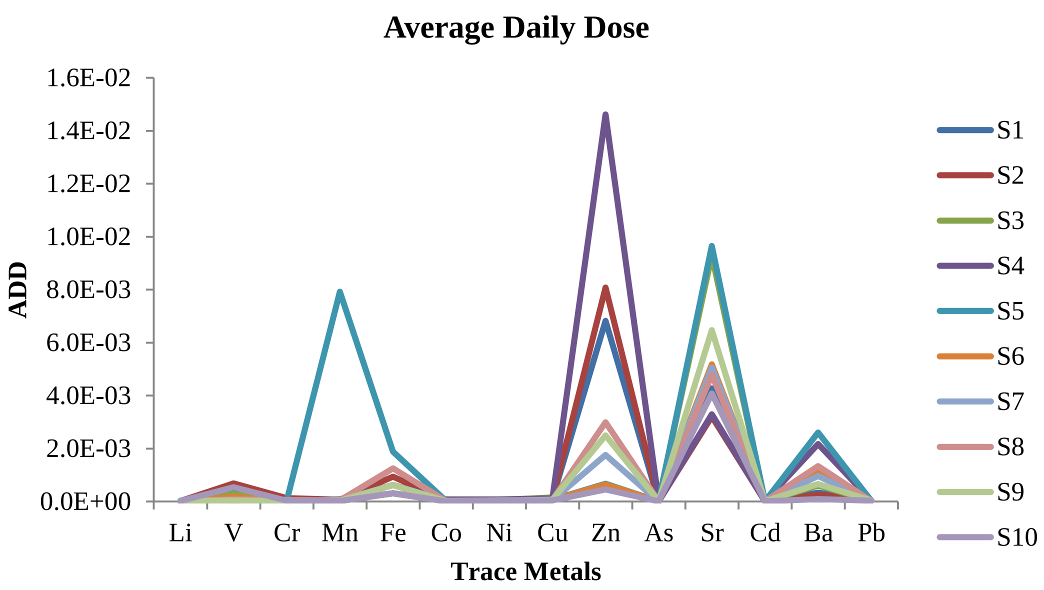

Figure 3: Average Daily Dose for Trace Metals through water intake in Limbe

Carcinogenic Risk (CR)

CR for the carcinogenic metals; Cr, Cd, Ni and As. **Table 7** and **Table 9**, showed that all metals were generally satisfactory **(Figure 4)**. CR values varied between 0.000016 and 0.00704. This implies that consumption of groundwater in this area is tolerable, with no cancer-related health problems.

Table 7: Carcinogenic Risk of Groundwater, Limbe

Sample ID	As	Cd	Cr	Ni
S_1 (Borehole) – Ngeme	8.5×10^{-5}	2.9×10^{-5}	0.001232	3.4×10^{-5}

S_2 (Borehole) – New Town	7.2 x 10^{-5}	3.2 x 10^{-5}	0.00704	5.7 x 10^{-5}
S_3 (Well) – Dockyard	8.7 x 10^{-4}	2.6 x 10^{-5}	0.000704	6.4 x 10^{-5}
S_4 (Well) – Motowoh	8.5 x 10^{-5}	4.5 x 10^{-5}	0.00264	1 x 10^{-4}
S_5 (Well) – New Market	1.5 x 10^{-4}	2.9 x 10^{-5}	0.001584	6.8 x 10^{-5}
S_6 (Well) – Alpha Club	6.5 x 10^{-5}	2.4 x 10^{-5}	0.001408	4.1 x 10^{-5}
S_7 (Well) – Espoir Road	2.6 x 10^{-5}	2.6 x 10^{-5}	0.000704	3.4 x 10^{-5}
S_8 (Well) – Bonadikombo	3.9 x 10^{-5}	2.4 x 10^{-5}	0.002816	4.9 x 10^{-5}
S_9 (Stream) – Bonadikombo	4.5 x 10^{-5}	1.6 x 10^{-5}	0.001056	3 x 10^{-5}
S_{10} (Spring) – Bosumbu	1.2 x 10^{-4}	2.4 x 10^{-5}	0.001584	3.4 x 10^{-5}
Maximum	**8.7 x 10^{-4}**	**4.5 x 10^{-5}**	**0.00704**	**1 x 10^{-4}**
Minimum	**2.6 x 10^{-5}**	**1.6 x 10^{-5}**	**0.000704**	**3 x 10^{-5}**

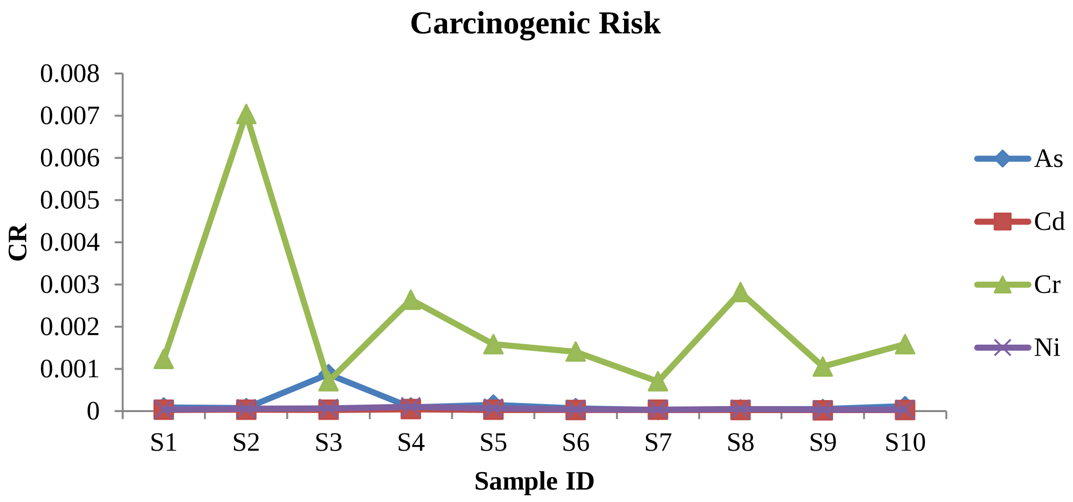

Figure 4: Carcinogenic Risk for Trace Metals in Groundwater, Limbe

Hazard Quotient (HQ) and Hazard Index (HI)

All samples were less than 1 for both HQ and HI, indicating they are safe **(Table 9)**. HQ varied between 0.0027 and 0.5657 and HI between 0.0171 and 0.5826. HI is a cumulative sum of all the HQ values. HI was in the order of S5 > S4 > S2 > S1 > S9 > S8 > S7 > S10 > S3 > S6 **(Table 8)**. There were no non-carcinogenic adverse effects.

Table 8: Hazard Quotients and Hazard Indices for Non-carcinogenic Metals

Sample ID	Hazard Quotient (HQ)						Hazard Index
	Mn	Fe	Cu	Zn	V	Pb	HI
S_1 (Borehole) – Ngeme	0.0034	0.0004	0.0027	0.0227	0.0066	0.0110	0.0468
S_2 (Borehole) - New Town	0.0047	0.0013	0.0027	0.0269	0.0097	0.0112	0.0566
S_3 (Well) – Dockyard	0.0016	0.0004	0.0038	0.0016	0.0041	0.0076	0.0191
S_4 (Well) – Motowoh	0.0061	0.0009	0.0030	0.0487	0.0004	0.0136	0.0727

S_5 (Well) - New Market	0.5657	0.0027	0.0018	0.0022	0.0007	0.0095	0.5826
S_6 (Well) - Alpha Club	0.0020	0.0009	0.0014	0.0022	0.0025	0.0082	0.0171
S_7 (Well) - Espoir Road	0.0038	0.0004	0.0010	0.0059	0.0007	0.0096	0.0214
S_8 (Well) – Bonadikombo	0.0034	0.0018	0.0013	0.0100	0.0011	0.0074	0.0249
S_9 (Stream) – Bonadikombo	0.0027	0.0009	0.0016	0.0083	0.0006	0.0116	0.0257
S_{10} (Spring) – Bosumbu	0.0013	0.0004	0.0011	0.0015	0.0076	0.0075	0.0196

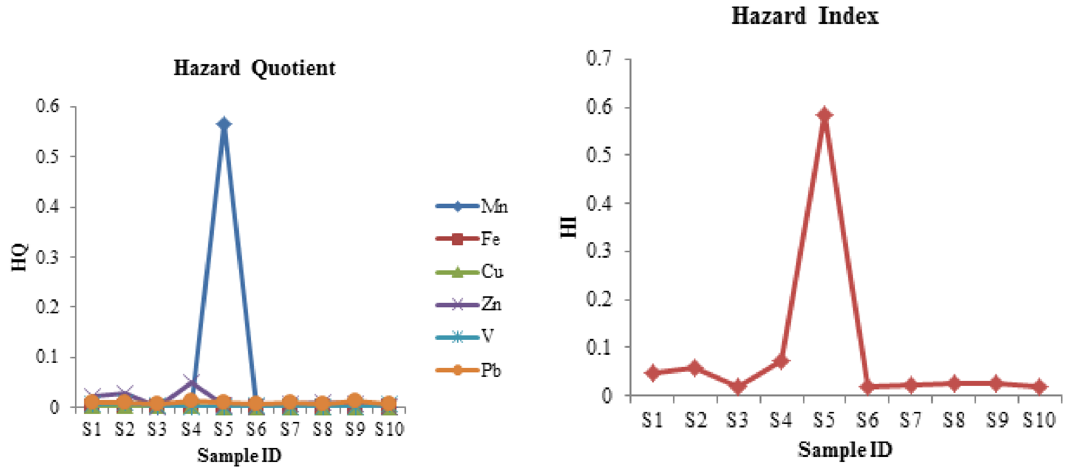

Figure 51: Non-carcinogenic hazards for trace metals through water intake in Limbe

Table 9: Summary Classification of Health Risk Assessment, Limbe.

Index	Range	Classification	Samples	%	Reference
CR	10^{-6} - 10^{-4} <	Generally satisfactory	10	100	[27]
HQ	<1	Acceptable level (no concern)	10	100	[32]
HI	<1	Safe	10	100	[32]

4.2.2 Pollution Risk Indices

Degree of Contamination (DC)

DC is revealed by estimation of the extent of trace metal pollution in the area. It ranged between 0.66 and 2.92 and in the order S5 (2.92) > S4 (1.91) > S3 (1.38) > S8 (1.29) > S6 (1.19) > S9 (1.10) > S7 (1.09) > S2 (0.99) > S1 (0.95) > S10 (0.66), with Sample 5 exhibiting the highest value **(Figure 6)**. According to classification [34], DC for all samples was less than 10 **(Table 10)**, indicating a low contamination factor.

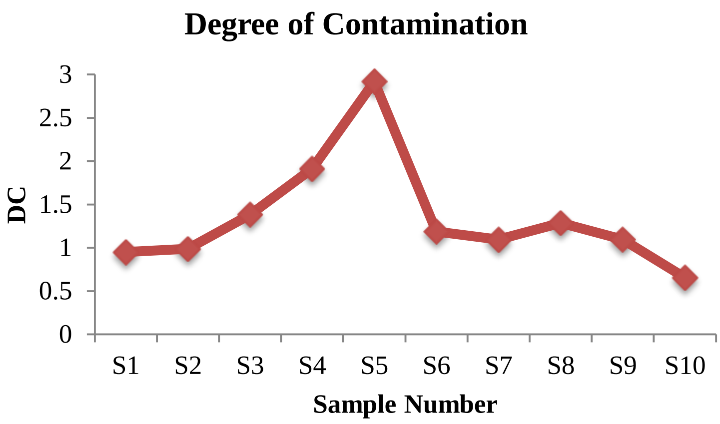

Figure 6: Degree of Contamination for Trace Metals in Groundwater, Limbe

Enrichment Factor (EF)

Strontium (Sr) was chosen as a stationary reference metal to perform this calculation to know the most enriched metal in Limbe. EF values < 2 indicate that the metal is entirely from natural processes; whereas EF values > 2 reveal that the sources are anthropogenic. Results revealed all metals except Zn were from natural processes, with an EF of 2.84 **(Figure 7)**. Zn therefore originated from anthropogenic actions on land, which could be linked to the use of fertilizers in agriculture especially with the presence of the Cameroon Development Corporation (CDC) in the study area. Zn was the most enriched trace metal in Limbe.

The sequence of EF in groundwater is Zn (2.84) > Fe (1.14) > Cu (1.14) > Mn (0.23) > Sr (0.23) > V (0.11) > Li (0.08) > Ni (0.04) > Ba (0.04) > Cr (0.03) > As (0.01) > Co (0.01) > Pb (0.005) > Cd (0.002).

From classification [35], one metal underwent moderate enrichment, minimal enrichment for two and eleven had background contaminations **(Table 11)**.

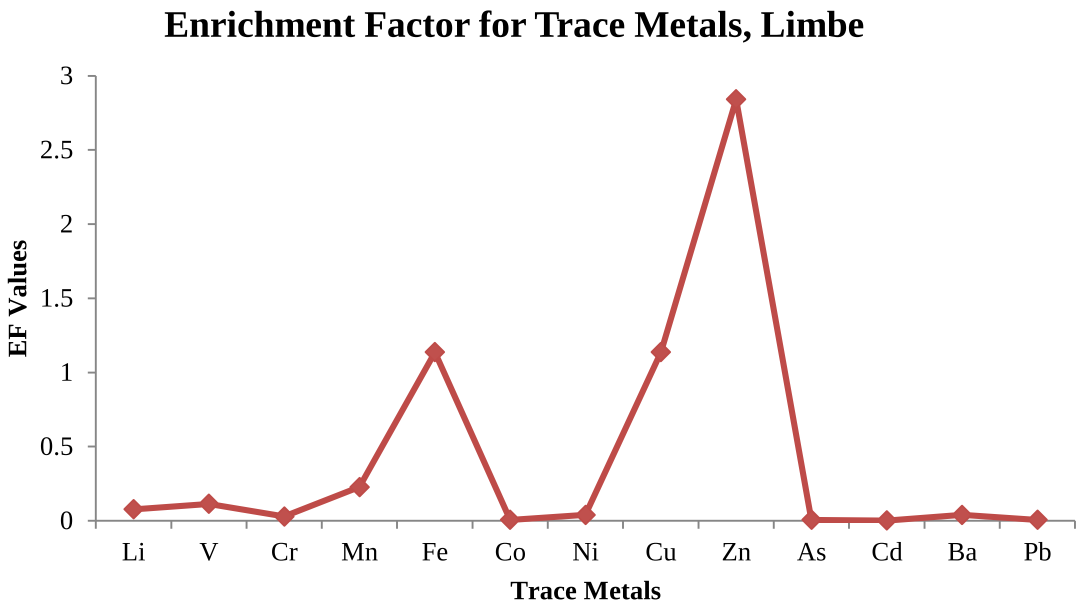

Figure 7: The Enrichment Factor for Trace Metals in Groundwater, Limbe

Ecological Risk Assessment

This gives results for both ecological risk factor and ecological risk index of the trace metals in the groundwater.

i. Ecological Risk Factor (ER)

ER ranged between 0.00292 and 1.7, with Cr at the peak of the chart **(Figure 8)**. All metals were less than 40. This explains low potential risk of trace metals in groundwater in Limbe.

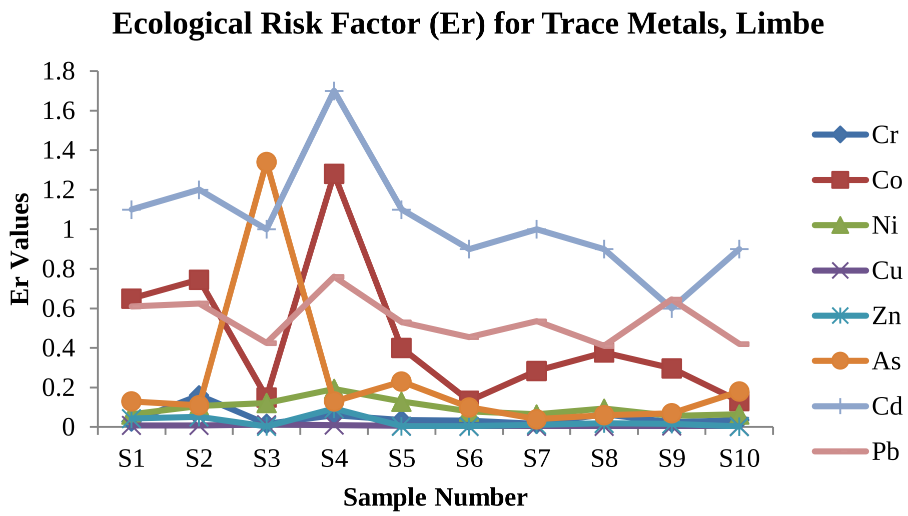

Figure 8: The Ecological risk factor for Trace Metals in Groundwater, Limbe

ii. Ecological Risk Index (RI)

All samples were less than 150 and showed low ecological risk indices. Sample 4 peaked the area with an index of 4.23, whereas Sample 6 indicated the lowest index value of 1.707 **(Figure 9)**.

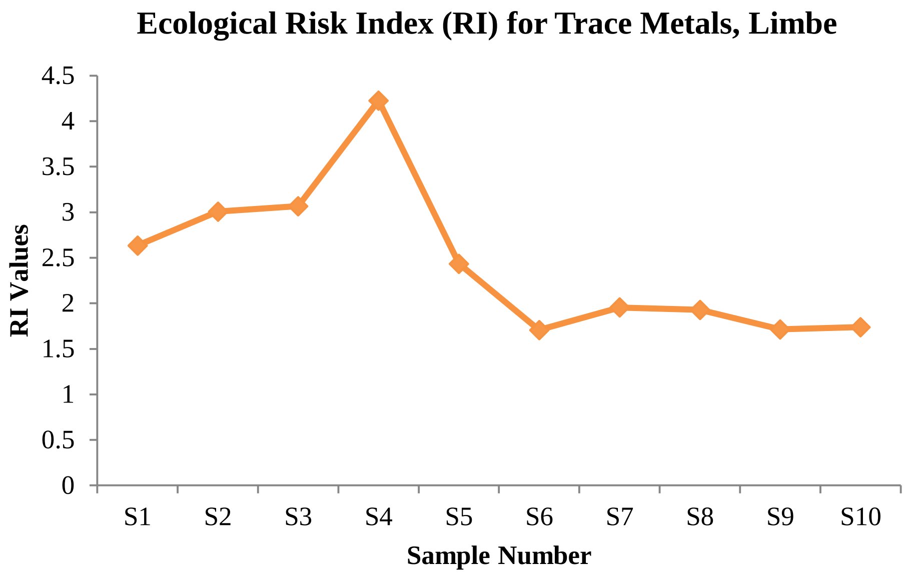

Figure 9: Ecological risk index for Trace Metals of groundwater in Limbe

Pollution Load Index (PLI)

The PLI values for groundwater varied between 0.037 and 0.014.Samples 5 and 10 respectively held the highest and lowest load indices **(Figure 10)**. All samples were less than 1, indicating that 100% of the trace metals in groundwater were unpolluted **(Table 11)**.

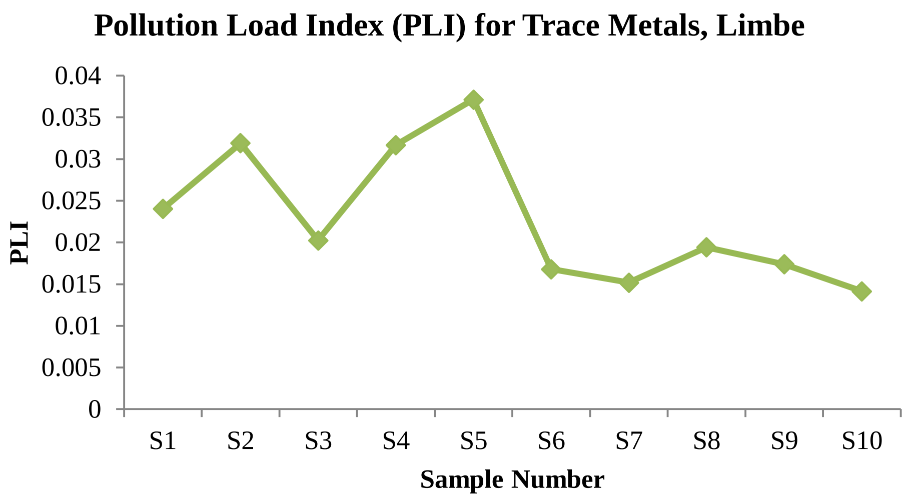

Figure 102: The Pollution Load Index for trace metal in Groundwater, Limbe

Geo-accumulation Index (Igeo)

The Igeo class for the trace metals in groundwater in Limbe were all less than 0 **(Table 10)**. According to [38] classification, the trace metals are unpolluted.

Table 10: Geo-Accumulation Index for Trace Metals in Goundwater, Limbe

Sample ID	Li	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Sr	Cd	Ba	Pb
S1	-8.97	-4.35	-6.74	-8.64	-8.23	-3.53	-6.87	-9.79	-5.11	-6.85	-2.14	-5.35	-3.31	-3.62
S2	-8.74	-3.79	-4.23	-8.16	-6.64	-3.33	-6.13	-9.79	-4.87	-7.09	-2.56	-5.23	-3.64	-3.58
S3	-9.97	-5.04	-7.55	-9.74	-8.23	-5.65	-5.95	-9.29	-8.93	-3.48	-1.02	-5.49	-2.47	-4.14
S4	-9.23	-8.55	-5.64	-7.80	-7.23	-2.55	-5.28	-9.62	-4.01	-6.85	-2.51	-4.73	-0.60	-3.30
S5	-8.38	-7.64	-6.38	-1.25	-5.64	-4.23	-5.87	-10.35	-8.45	-6.03	-0.97	-5.35	-0.34	-3.82
S6	-9.97	-5.77	-6.55	-9.38	-7.23	-5.82	-6.58	-10.70	-8.50	-7.23	-1.86	-5.64	-1.47	-4.04
S7	-9.55	-7.64	-7.55	-8.46	-8.23	-4.72	-6.87	-11.17	-7.06	-8.55	-1.90	-5.49	-1.77	-3.81
S8	-11.55	-6.91	-5.55	-8.64	-6.23	-4.31	-6.34	-10.87	-6.30	-7.97	-1.98	-5.64	-1.31	-4.19
S9	-8.97	-7.74	-6.97	-8.97	-7.23	-4.66	-7.04	-10.55	-6.56	-7.74	-1.54	-6.23	-2.31	-3.54
S10	-9.23	-4.14	-6.38	-9.97	-8.23	-5.84	-6.87	-11.07	-9.00	-6.38	-2.21	-5.64	-5.08	-4.16
Minimum	**-11.55**	**-8.55**	**-7.55**	**-9.97**	**-8.23**	**-5.84**	**-7.04**	**-11.17**	**-9.00**	**-8.55**	**-2.56**	**-6.23**	**-5.08**	**-4.19**
Maximum	**-8.38**	**-3.79**	**-4.23**	**-1.25**	**-5.64**	**-2.55**	**-5.28**	**-9.29**	**-4.01**	**-3.48**	**-0.97**	**-4.73**	**-0.34**	**-3.30**
Mean Igeo	**-9.45**	**-6.16**	**-6.35**	**-8.10**	**-7.31**	**-4.46**	**-6.38**	**-10.32**	**-6.88**	**-6.82**	**-1.87**	**-5.48**	**-2.23**	**-3.82**

Table 11: Summary Classification of Pollution Indices in Groundwater, Limbe.

Index	Range	Classification	Samples	%
DC	< 10	low degree of contamination factor	10	100
	≤ 1	Background contamination	11	78.57
EF	1 – 2	Minimal enrichment	2	14.29
	2– 5	Moderate enrichment	1	7.14
Er	Er <40	Low potential risk	10	100
RI	RI < 150	low ecological risk	10	100
PLI	<1	No pollution	10	100
Igeo	≤ 0	Unpolluted	10	100

Pearson's Bivariate Correlation Analysis between Trace Metals and Physicochemical Parameters

An established relationship in the form of a correlation matrix between trace metals and physicochemical parameters correlates two classes; either between metal and metal or metal and physicochemical parameter. Positive values indicate a positive relationship while negative values of r indicate an inverse relationship [40]. Ranges for r values used in this study were between 0.50 and 0.64 (significant); 0.65 and 0.79 (strong or moderate); 0.80 and 0.89 (very strong); >0.9 (near perfect to perfect). A strong correlation existed between Mn/Li, Sr/Mn, Sr/Zn, Sr/As, Ba/Mn, Ba/Fe, Ba/V, Ba/Ni, Cd/Fe, Ni/Co, Zn/Ni, EC/Cu, EC/Sr, EC/Ba, TDS/Cu, TDS/Sr, TDS/Ba, Temp/Ba and As/Cu; very strong correlation between Fe/Mn, Cd/Mn, Cd/Co, Cd/Ni, Cd/Zn, Pb/Co and Pb/Zn and a near perfect correlation between Zn/Co, As/TDS, and As/EC. No correlation between pH/Cr, Temp/Cr and Co/V **(Table 12)**.

Table 12: Correlation Matrix of r values for Trace Metals and Physicochemical Parameters Limbe

	Li	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Sr	Cd	Ba	Pb	Temp	pH	EC	TDS
Li	1																	
V	0.21	1																
Cr	0.22	0.53	1															
Mn	0.63	-0.28	-0.09	1														
Fe	0.37	-0.29	0.31	**0.80**	1													
Co	0.29	-0.01	0.48	-0.04	0.10	1												
Ni	0.13	-0.24	0.27	0.27	0.32	0.70	1											
Cu	0.13	0.26	0.19	-0.08	-0.16	0.46	0.59	1										
Zn	0.17	0.07	0.49	-0.24	-0.06	**0.98**	0.62	0.47	1									
As	-0.20	0.10	-0.25	-0.01	-0.22	-0.27	0.25	0.67	-0.26	1								
Sr	0.17	-0.37	-0.49	0.63	0.36	-0.48	0.07	0.18	-0.60	0.62	1							
Cd	0.20	0.02	0.35	**0.81**	0.067	**0.86**	**0.84**	0.53	**0.82**	-0.01	-0.32	1						
Ba	0.18	**-0.73**	-0.12	0.68	0.68	0.34	0.66	-0.03	0.19	-0.13	0.34	0.44	1					
Pb	0.51	-0.10	0.29	-0.03	-0.03	**0.83**	0.42	0.34	**0.82**	-0.35	-0.35	0.56	0.22	1				
Temp	0.13	-0.52	0.01	0.47	0.49	0.22	0.53	0.39	0.11	0.27	0.53	0.30	0.66	0.22	1			
pH	-0.07	-0.54	0.00	-0.18	0.09	0.41	0.16	-0.16	0.42	-0.40	-0.24	0.03	0.25	0.53	-0.01	1		
EC	-0.04	0.08	-0.27	0.17	-0.08	-0.33	0.21	0.62	-0.35	**0.98**	**0.75**	-0.08	**-0.78**	-0.36	0.31	-0.41	1	
TDS	-0.04	0.08	-0.27	0.17	-0.08	-0.33	0.21	0.62	-0.35	**0.98**	**0.75**	-0.08	**-0.78**	-0.36	0.31	-0.41	1	1

Hierarchical Cluster Analysis (HCA) of Trace Metals

The dendrogram **(Figure 11)** was made up of two clusters, each with two classes. Cluster I had two classes; Zn and Sr. Zn is the soluble and Sr is enriched. Cluster II had 13 non soluble elements. This cluster had two class divisions; Class I contains 9 elements, which included As, Cd, Li, Co, Pb, Ni, Cr, Cu and V. They are the less enriched. Class II had 3 elements; Fe, Ba, and Mn. This is the moderately enriched class.

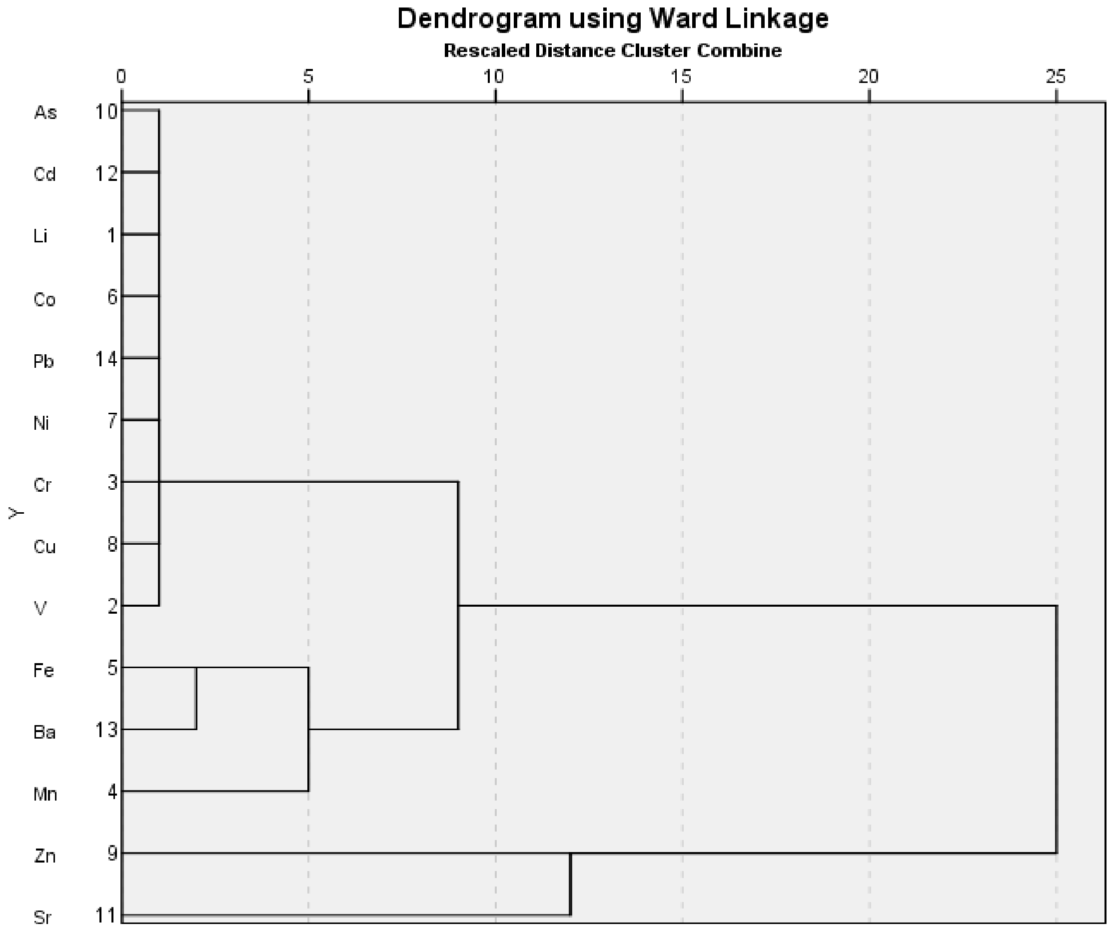

Figure 11: Dendrogram for Trace Metals in Groundwater, Limbe

5. CONCLUSIONS

Trace metals in Limbe have geogenic and anthropogenic sources. Trace metal concentrations are all below acceptable limits but for the concentration of Ba at New-Market Street, whose concentration is above acceptable limits but are all below harmful levels. The metal with the highest average daily intake in Limbe and environs is Zn. Generally, groundwater in Limbe and environs is unpolluted. Health risk indices show that groundwater is generally satisfactory and safe for consumption and poses no carcinogenic risk. All metals except Zn are from natural processes. Zn is the most enriched trace metal. Some element pairs exhibit correlation, amongst with exists a near perfect correlation between Zn and Co. Because of the heterogeneity of aquiferous formations that is frequently impacted by human actions on land and occasionally by natural processes, it is of utmost importance to periodically monitor and evaluate the concentrations of these metals in groundwater to curb future pollution and health risks in Limbe and environs.

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