



# Trace Metals in Groundwater of the South Eastern Piedmont Region of Mount Cameroon: Quantification and Health Risk Assessment

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## Abstract

The South Eastern Piedmont Region of Mount Cameroon is getting increasingly populated. Groundwater is the main resource for drinking in this area; hence, the quantification of trace metals, suitability and quality of the groundwater resources for drinking, domestic and agro-industrial uses is of public and scientific concern. In this study, 10 samples were collected from 10 sites in September 2017. Field measurement of physicochemical parameters and investigation of the levels of trace metal content in groundwater was determined using Inductively Coupled Plasma Mass Spectroscopy ICP-MS. R-mode statistical analysis has been done and traces metals elements correlated with the physicochemical parameters and cluster analysis PCA carried out. The paper also highlights and determines the average daily dose ADD, the carcinogenic risks CR and the non-carcinogenic risk hazard quotient HQ which yields the hazard indices HI. The general trend of mean trace metal concentration in the sampled groundwater was in the order of: Zn > Fe > Al > V > Mn > Cu > Cr > Ni > Pb > As > Co > Cd > Sb. All the groundwater risk indices; ADD, CR, HQ and HI were less than 1 in categories of insignificant health risk. The severity of metal toxicity is governed by several factors, such as dose, nutrition, age, and even life style. Therefore, this low trend might not guarantee the complete absence of human health risk. Generally, from risk assessment on trace metals using risk indices, the analyzed water samples might not be at an alarming health risk. However, due to an increasing level of environmental pollution that might be imposed by increasing human activity in this region, water sources might become a potential sink of contaminants; this is significant reason that makes constant monitoring, implementation and treatment of groundwater for drinking purposes obligatory.

## Subject Areas

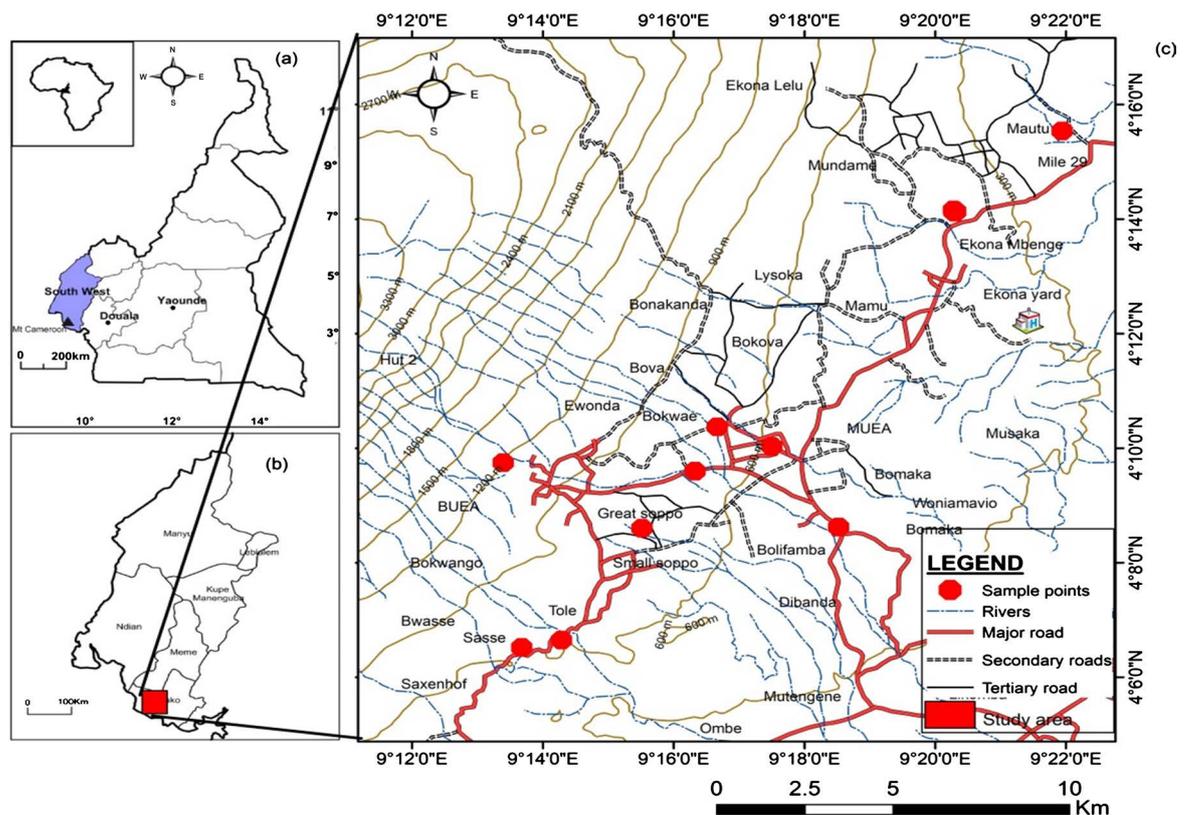
Geology, Hydrology, Environment-Science

## Keywords

Trace-Metal, Assessment, Pollution-Indices, Health-Risks, Environmental-Pollution, Mount-Cameroon

## 1. Introduction

This study area is situated between  $4.2667^{\circ}$  -  $4.8417^{\circ}$  N and  $9.3333^{\circ}$  -  $9.3694^{\circ}$  E at the foot of Mount Cameroon at an elevation of 570 - 860 m above mean sea level within a surface area of 270 km<sup>2</sup> as shown in **Figure 1**. The presence of trace metal species in groundwater can be of geogenic or anthropogenic origins. The constituents present may pose many health risks to human and other life when they exceed the maximum contamination levels. Because of the absence of treatment of groundwater before drinking in the piedmont regions of Mount Cameroon, it is mandatory to assess the trace metal content, and to keep regular drinking water monitoring programs. Thus the objective of this study is to examine and highlight the levels of twelve metals in spring sources in this region of Cameroon. The paper also reveals the correlation coefficients between



**Figure 1.** Location map for measurements and sample collection: Piedmont region of mount Cameroon.

the analyzed parameters, the estimate of the degree of metal contamination hazards and pollution indices. The South Eastern Piedmont region of Mount Cameroon has numerous institutions of higher learning, administrative offices and Water bottling companies supplying the nation and exported to neighboring countries (Tchad, Nigeria, Equatorial Guinea and Gabon). Also it is an agro-industrial production zone of banana, palm oil, pawpaw, tomatoes water melon and pineapple, all of which are exported and rely on groundwater. The evaluation of the trace metal content of groundwater in this region is a vital necessity for Cameroonian and international concerns as to the quality of the exported products. The presence of the above institutions and agroindustries has led to unprecedented population growth and urbanization around this area resulting in a high demand for water that has now exceeded supply. The consequence is a greater exploitation of groundwater resources, which is the only available and reliable water source in this area for drinking, agricultural and industrial purposes [1]. The heavy metal quality of spring water that is exploited for consumption by more than 80% of inhabitants of this area is unknown. Thus a plethora of health risks associated with elevated trace metals concentrations in groundwater and soils around Mt. Cameroon respectively would arise if the trace metal concentrations of groundwater in this area is high [2] [3].

Trace metals are chemical components found in low concentrations, in mass fractions of ppm or less, in water, organisms and soil [4]. 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 [5]. 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 [6] [7].

Health risk assessment involves four steps: Hazard identification, dose-response assessment, exposure assessment, and risk characterization. Trace metals are naturally part of the environment and can be found in soils and rocks and also dissolved in rivers, streams and groundwater. Volcanic activities, domestic, agricultural, medical and technological applications have led to the wide distribution of trace metals into the environment; raising concerns over their potential effects on human health and the environment. The piedmont region of mount Cameroon, where numerous spring, streams and rivers around Fako take their rise is dominantly made up of overlapping lava flows of alkaline basalt composition, with a lesser but probably significant proportion of pyroclastic [8] [9].

Water is one of the essentials that support all form of animal and plant life [10] and it is generally obtained from two principal natural sources; Surface water such as fresh water lakes, rivers and streams and groundwater such as springs and well water. Groundwater comes into contact with rocks (alkaline basalts and pyroclastics) and their weathering products, soils. By ion exchange, precipitation, dissolution or mixing, trace metal ions contained in the rocks are introduced into the wa-

ter. These metals exist in water as colloidal, particulate and dissolved species [11]. 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.

### 1.1. Climate

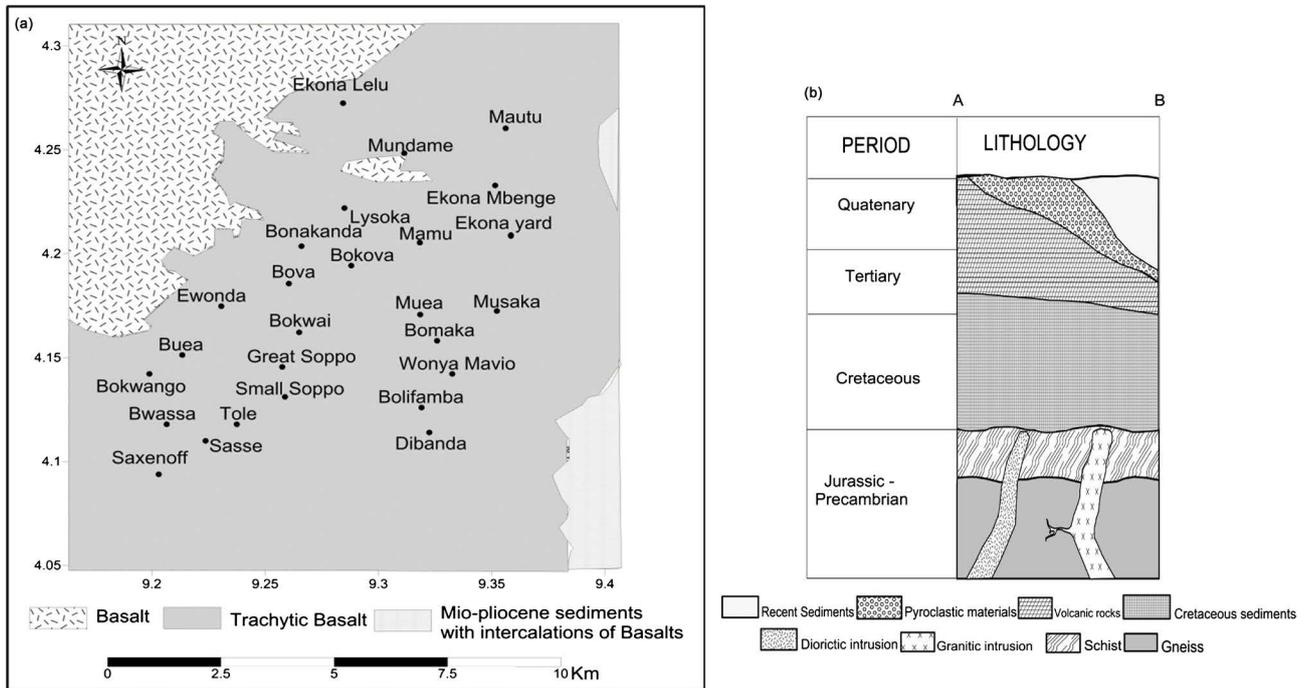
The study area experiences two distinct seasons: a rainy season that begins in April and ends in October with a high annual rainfall between 3000 - 5000 mm, and a dry season that begins in November and ends in March [12] [13]. Daily temperatures range from 17°C - 34°C annually.

### 1.2. Hydrology and Hydrogeology

The area is characterized by a hilly topography, a dense network of springs, streams and high humidity. Due to the fact that tectonics associated with volcanism creates fracturing and faulting that runs over long distances, the formations of the piedmont regions low-lying besides the volcanic relief have deep joints, fractures, and faults, which because of their abundance and connectivity can retain large volumes of running water in underground channels that surge out down slope as large springs [1] [14] [15]. Mt Cameroon is made up of unwelded scoria or pyroclastic materials that are porous and therefore make up good aquifers with an enormous water-holding capacity [1]. Hydrogeologically, the area is made of admixtures of various layers of volcanics fractured massive basaltic rocks with serious aquiferous potentials found mainly in fractures. At various hill sides where the overlying more permeable formations and less permeable formations are crosscut by topography or where fractures are exposed on the surface, springs occur. Also, at the lower slopes where impermeable massive basaltic lava flows or strata outcrop on the surface, springs emerge at the top of the impervious or impermeable strata [16]. This area has three principal water service providers: Camerounaise Des Eaux, CDE, Community Water Schemes CWS and private boreholes, BH.

### 1.3. Geology

Mount Cameroon is an elliptical shaped strato-volcano approximately 4095 m above mean sea level and forms part of the Cameroon Volcanic Line, CVL [18]. This line is made up of 12 main volcanic centres with ages ranging from 51.8 Ma to the Present [19] [20]. The volcanic rocks of Mt Cameroon with the exception of the nephelinite series of Mt. Etinde are typically alkaline. The lithological sequence of the differentiated alkaline series is complete and includes basaltic lavas (alkali basalts, picrites and hawaiites), intermediate lavas; mugearites and benmoreites, and felsic lavas; phonolites, trachytes, and alkali rhyolites. The general geology of Mt Cameroon is represented by a Precambrian metamorphic basement; schists and gneisses intruded by granite, diorites [21]. The basement is covered by cretaceous to quaternary sediments, observable in the Bomana maar at the NW of the massif [22] [23] as shown in **Figure 2(a)** and **Figure 2(b)**.



**Figure 2.** (a) Geologic map of study area made up of 3 rock types; trachyte, basalt and miopliocene sediments with intercalations of basalt. (b) Lithostratigraphic section showing metamorphic basement, schists and gneisses intruded by granite, diorites and overlain by Cretaceous sediments, volcanic rocks pyroclastic materials and weathered sediments.

## 2. Materials and Methods

### 2.1. Sample Collection, Pre-Treatment and Chemical Analysis

Ten groundwater samples were collected from 10 pre-selected springs. Site selection was based on spatial distribution of the springs, population and location of agro-industries. At each site, groundwater temperature, electrical conductivity and pH value were measured in situ, using the portable field pH, EC and TDS meters presented in **Table 1**.

Prior to sampling, the pre-cleaned sample bottles were rinsed with the sample water. The spring water was withdrawn with the use of a 50 ml syringe, and then filtered through the 0.2  $\mu\text{m}$  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. Questionnaire Administration

A total of one thousand questionnaires were administered. One hundred randomly issued to households at each sampling location and assisted in filling by field workers. Population subgroups were investigated in seven main categories; area, gender, age, body weight, water source, daily intake and longevity of use. However, since trace metals concentrations were not measured in water drunk

**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 and marker | 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                           |

away from home, exposure away from home was estimated by assuming equal concentrations at home and away. Dietary exposure due to use of drinking water in hot or cold beverages and food items such as; food, breast milk, soups was not determined. The family members of respondents (various ages) were weighed using a Taylor medical weighing balance.

### 2.3. Human Health Risk Assessment

Human health risk assessment is considered as the characterization of the potential adverse health effects of humans as a result of exposures to environmental hazards and the processes of estimating the health effects that might result from exposure to carcinogenic and noncarcinogenic chemicals [24]. This process employed engineering/science tools and statistics to identify and measure hazards, determine possible routes of exposure, and finally use that information to calculate a numerical value to represent the potential risk [25]. The risk assessment process as proposed by the US Environmental Protection Agency consists of four steps [26]. These steps include: 1) Hazard identification, 2) Exposure assessment, 3) Dose response/toxicity assessment and 4) Risk characterization.

#### 2.3.1. Hazard Identification:

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 [27] [28] as presented in **Table 2**.

**Table 2.** Trace metals and their effects.

| Component | Toxicity effects [29]   |
|-----------|---|
| 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 <sup>+6</sup> 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.                      |

### 2.3.2. Exposure Assessment

This is the process of measuring or estimating the intensity, frequency and duration of human exposures to an environmental agent [27]. 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 intakes of metals through ingestion of groundwater were calculated using Equation (1) [29].

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

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 [29].

### 2.3.3. 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.

#### 2.3.4. 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.

#### 2.3.5. 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 [24]. 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) [24] [30] [31].

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

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

#### 2.3.6. 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) [32].

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

$RfD$  is the reference dose  $\text{mg}/\text{kg}/\text{d}$ . It represents a toxicity index of a daily exposure to the population in comparison to a safe level of exposure orally over a lifetime [33].

#### 2.3.7. Harzard Index (HI)

Harzard index (HI) is the toxic risks due to all the potentially hazardous substances present in the same media simultaneously [26]. 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) [32].

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

### 3. Results and Discussion

#### 3.1. Field Measured Physicochemical Parameters

Field physicochemical parameters EC, pH, TDS and Temperature were measured and presented in **Table 3**. EC ranged from 128 - 290  $\mu\text{S/cm}$ , pH from 6.2 - 6.9, TDS from 85.8 - 194.3 mg/L and temperature from 18.5°C - 22.9°C.

#### 3.2. Body Weight and Water Intake

The ranges of measured mean body weights and the ranges of mean daily water intakes from 1000 questionnaires; 100 households per location in the various age groups presented in **Table 4**, was used to determine the various risk and hazard indices.

#### 3.3. Trace Metals Concentrations in Groundwater at Various Locations of Study Area

The results for ten water samples of trace metal analysis ICP-MS are presented in **Table 5**. The concentrations of thirteen trace metals; Zn, Pb, Co, Cu, Cr, Mn, Cd, V, Fe, Ni, As, Sb, Al, Mn, and Pb were evaluated. All concentrations of these trace metals are below the WHO allowable limits and as such will not cause any immediate harm to consumers. However, the cumulative effects of long term consumption of these trace metals in the groundwater necessitated a health risk assessment.

Groundwater trace metal concentrations detected in samples varied within the

**Table 3.** Field determined physicochemical parameters; electrical conductivity (EC), pH, total dissolved solids (TDS) and temperature of groundwater in study area.

|            | N         | E        | EC $\mu\text{S/cm}$ | PH  | TDS mg/L | Temp °C |
|------------|-----------|----------|---------------------|-----|----------|---------|
| UPPERFARMS | 9.2232222 | 4.162472 | 128.0               | 6.2 | 85.8     | 18.5    |
| SASSE      | 9.2279444 | 4.108667 | 190.0               | 6.6 | 127.3    | 21.5    |
| TOLE       | 9.2380833 | 4.110806 | 209.0               | 6.8 | 140.0    | 21.1    |
| SANDPIT    | 9.2586111 | 4.143361 | 245.0               | 6.7 | 164.2    | 21.5    |
| BONDUMA    | 9.2721389 | 4.159972 | 207.0               | 6.8 | 138.7    | 22.7    |
| BWITEVA    | 9.2778056 | 4.172889 | 290.0               | 6.8 | 194.3    | 21.4    |
| MUEA       | 9.29175   | 4.167167 | 258.0               | 6.9 | 172.9    | 22.1    |
| MILE 16    | 9.3087222 | 4.143722 | 248.0               | 6.9 | 166.2    | 22.9    |
| EKONA      | 9.338     | 4.236    | 270.0               | 6.7 | 180.9    | 22.8    |
| MAUTU      | 9.3656944 | 4.258972 | 271.0               | 6.7 | 181.6    | 22.8    |
| Min        |           |          | 128.0               | 6.2 | 85.8     | 18.5    |
| Max        |           |          | 290.0               | 6.9 | 194.3    | 22.9    |
| Mean       |           |          | 227.8               | 6.7 | 152.6    | 21.6    |

**Table 4.** Mean Body weight BW, age-group Y and oral water intake WI.

| AGE     | 0 - 5 Y   |            | 6 - 10 Y  |           | 11 - 15 Y |         | 16 - 20 Y |         | 21 - 25 Y |         |
|---------|-----------|------------|-----------|-----------|-----------|---------|-----------|---------|-----------|---------|
| WEIGHT  | BW (Kg)   | WI (L)     | BW (Kg)   | WI (L)    | BW (Kg)   | WI (L)  | BW (Kg)   | WI (L)  | BW (Kg)   | WI (L)  |
| UPFARMS | 4.5 - 15  | 0.5 - 1    | 19 - 30   | 0.5 - 2   | 32 - 55   | 1.0 - 4 | 42 - 85   | 1.0 - 5 | 57 - 85   | 1.0 - 5 |
| SASSE   | 4.5 - 15  | 0.25 - 2   | 18 - 33   | 0.5 - 3   | 39 - 52   | 1.0 - 3 | 45 - 62   | 1.0 - 5 | 60 - 83   | 1.0 - 5 |
| TOLE    | 4.5 - 12  | 0.25 - 2   | 16 - 37   | 1.0 - 2   | 30 - 50   | 1.0 - 2 | 54 - 65   | 1.0 - 5 | 60 - 70   | 1.0 - 3 |
| SANDPIT | 5.5 - 14  | 0.25 - 5   | 19 - 32   | 0.5 - 1.5 | 32 - 55   | 1.0 - 2 | 40 - 60   | 1.0 - 3 | 52 - 71   | 1.0 - 5 |
| BONDUMA | 5.5 - 12  | 0.25 - 1   | 18 - 37   | 1.0 - 3   | 40 - 51   | 1.0 - 3 | 50 - 61   | 1.0 - 5 | 60 - 72   | 1.0 - 5 |
| BWITEVA | 5.0 - 12  | 0.25 - 1.5 | 25 - 41   | 1.0 - 5   | 45 - 53   | 1.0 - 3 | 56 - 63   | 1.0 - 5 | 60 - 70   | 1.0 - 5 |
| MUEA    | 4.6 - 12  | 0.25 - 1   | 18 - 37   | 0.5 - 2.5 | 39 - 84   | 1.0 - 2 | 50 - 65   | 1.0 - 5 | 60 - 70   | 1.0 - 3 |
| MILE 16 | 5.0 - 19  | 0.25 - 1.5 | 21 - 65   | 0.5 - 2   | 37 - 55   | 1.0 - 3 | 56 - 65   | 1.0 - 5 | 58 - 88   | 1.0 - 5 |
| EKONA   | 7.2 - 15  | 0.25 - 1   | 20 - 31   | 1.0 - 2   | 45 - 56   | 1.0 - 2 | 57 - 60   | 1.0 - 2 | 62 - 70   | 1.0 - 5 |
| MAUTU   | 3.9 - 16  | 0.25 - 2   | 18 - 39   | 1 - 1.5   | 40 - 75   | 1.0 - 3 | 51 - 60   | 1.0 - 3 | 60 - 78   | 1.0 - 3 |
| AGE     | 26 - 30 Y |            | 31 - 35 Y |           | 36 - 40 Y |         | 41 - 45 Y |         | >45       |         |
| WEIGHT  | BW (Kg)   | WI (L)     | BW (Kg)   | WI (L)    | BW (Kg)   | WI (L)  | BW (Kg)   | WI (L)  | BW (Kg)   | WI (L)  |
| UPFARMS | 63 - 90   | 1.0 - 5    | 65 - 90   | 1.0 - 5   | 65 - 90   | 1 - 5L  | 60 - 105  | 1.0 - 4 | 60 - 90   | 1 - 3L  |
| SASSE   | 60 - 80   | 1.0 - 5    | 45 - 92   | 1.0 - 3   | 77 - 85   | 2.0 - 5 | 70 - 85   | 1.0 - 3 | 64 - 85   | 2.0 - 5 |
| TOLE    | 60 - 72   | 1.0 - 5    | 60 - 90   | 1.0 - 4   | 65 - 91   | 1.5 - 5 | 70 - 82   | 1.0 - 5 | 60 - 85   | 1.0 - 3 |
| SANDPIT | 63 - 84   | 1.0 - 5    | 60 - 90   | 2.0 - 5   | 75 - 80   | 1.0 - 2 | 65 - 102  | 1.0 - 5 | 60 - 95   | 2.0 - 5 |
| BONDUMA | 60 - 75   | 1.0 - 5    | 62 - 76   | 1.0 - 5   | 60 - 83   | 1.0 - 5 | 65 - 95   | 1.0 - 4 | 67 - 80   | 1.0 - 5 |
| BWITEVA | 60 - 85   | 1.0 - 3    | 65 - 85   | 1.0 - 5   | 60 - 85   | 1.0 - 5 | 55 - 95   | 1.0 - 5 | 55 - 80   | 1.0 - 2 |
| MUEA    | 58 - 77   | 1.5 - 3    | 60 - 87   | 1.0 - 5   | 65 - 95   | 2.0 - 5 | 65 - 84   | 1.0 - 5 | 63 - 70   | 1.0 - 3 |
| MILE 16 | 64 - 72   | 1.0 - 3    | 60 - 80   | 1.0 - 5   | 60 - 83   | 1.0 - 5 | 64 - 90   | 1.0 - 5 | 68 - 85   | 1.5 - 2 |
| EKONA   | 65 - 86   | 1.0 - 3    | 63 - 80   | 1.0 - 5   | 62 - 75   | 2.0 - 4 | 65 - 95   | 1.0 - 5 | 65 - 85   | 1.0 - 4 |
| MAUTU   | 60 - 98   | 1.0 - 5    | 62 - 77   | 1.0 - 5   | 60 - 82   | 1.0 - 5 | 65 - 92   | 1.0 - 5 | 60 - 90   | 2.0 - 5 |

**Table 5.** Trace metal concentration and basic statistics of groundwater in study area.

| Location  | N     | E     | Zn µg/L | Pb µg/L | Co µg/L | Cu µg/L | Cr µg/L | Mn µg/L | Cd µg/L | V µg/L | Fe µg/L | Ni µg/L | As µg/L | Sb µg/L | Al µg/L |
|-----------|-------|-------|---------|---------|---------|---------|---------|---------|---------|--------|---------|---------|---------|---------|---------|
| Upfarms   | 9.223 | 4.162 | 8.5     | 0.74    | 0.06    | 1.7     | 0.7     | 4.3     | 0.06    | 4      | 20      | 0.6     | 0.04    | 0       | 17      |
| Sasse     | 9.228 | 4.109 | 19.7    | 0.31    | 0.03    | 1.1     | 1.2     | 1.9     | 0.02    | 9.5    | 5       | 0.7     | 0.15    | 0       | 11      |
| Tole      | 9.238 | 4.111 | 44.3    | 0.4     | 0.07    | 1.2     | 1       | 2.9     | 0.11    | 10.7   | 20      | 0.7     | 0.18    | 0       | 32      |
| Sandpit   | 9.259 | 4.143 | 31.6    | 0.32    | 0.04    | 0.8     | 1.1     | 2.1     | 0.01    | 12.8   | 10      | 0.4     | 0.11    | 0       | 9       |
| Bonduma   | 9.272 | 4.160 | 9.1     | 0.18    | 0.14    | 1       | 0.9     | 3.1     | 0.01    | 7.2    | 5       | 0.5     | 0.08    | 0       | 9       |
| Bwiteva   | 9.278 | 4.173 | 13.6    | 0.22    | 0.05    | 1       | 1.1     | 2.8     | 0.01    | 13.3   | 5       | 0.5     | 0.2     | 0       | 9       |
| Muea      | 9.292 | 4.167 | 17.7    | 0.21    | 0.07    | 1       | 1.2     | 5.2     | 0.02    | 13.7   | 5       | 0.6     | 0.15    | 0       | 6       |
| Mile 16   | 9.309 | 4.144 | 26.4    | 0.28    | 0.11    | 1.8     | 1.7     | 5.9     | 0.02    | 17.2   | 5       | 0.6     | 0.2     | 0       | 12      |
| Ekona     | 9.338 | 4.236 | 18      | 0.26    | 0.04    | 1.7     | 1       | 1.9     | 0.01    | 13.8   | 30      | 0.4     | 0.19    | 0       | 14      |
| Mautu     | 9.366 | 4.259 | 13.3    | 0.23    | 0.03    | 1       | 1.1     | 1.4     | 0.01    | 15.3   | 5       | 0.5     | 0.16    | 0       | 8       |
| Min       |       |       | 8.5     | 0.18    | 0.03    | 0.8     | 0.7     | 1.4     | 0.01    | 4      | 5       | 0.4     | 0.04    | 0       | 6       |
| Max       |       |       | 44.3    | 0.74    | 0.14    | 1.8     | 1.7     | 5.9     | 0.11    | 17.2   | 30      | 0.7     | 0.2     | 0       | 32      |
| Mean      |       |       | 21.25   | 0.34    | 0.07    | 1.24    | 1.12    | 3.23    | 0.03    | 11.56  | 12.08   | 0.55    | 0.14    | 0       | 13.75   |
| WHO limit |       |       | 3000    | 10      | 10      | 2000    | 50      | 400     | 3       | 200    | 2000    | 70      | 10      | 20      | 200     |

study area. Average concentrations of these elements were in the decreasing order as follows in mg/l: Zn (0.0202), Fe (0.02), Al (0.0127), V (0.0117), Mn (0.0032), Cu (0.00123), Cr (0.0011), Ni (0.00055), Pb (0.00032), As (0.00015), Co (0.0000666), Cd (0.0000325), Sb (0.000024). Zn, Pb, Co, Cu, Cr, Mn, V, Ni, As, Sb and Al were detected in all the groundwater samples. The highest concentration of trace metal found in the study area was of Zn with a maximum of 44.3 µg/L detected at Tole.

### 3.4. Pearson's Correlation Analysis (PCA) between Trace Metals

Correlation between trace metals in groundwater within the study area was carried out using Pearson's correlation analysis (PCA) shown in **Table 6**, to establish the relationships that exist between the variables; trace metals and the physicochemical parameters 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; Fe and Cu ( $r = 0.843$ ), Fe and Sb ( $r = 0.816$ ), Cr and V ( $r = 0.778$ ), Cd and Al ( $r = 0.930$ ), V and As ( $r = 0.817$ ), V and EC ( $r = 0.867$ ), V and PH ( $r = 0.718$ ), V and TDS ( $r = 0.867$ ), V and temperature ( $r = 0.724$ ), As and EC ( $r = 0.749$ ), As and TDS ( $r = 0.749$ ), EC and TDS ( $r = 1$ ), TDS and PH ( $r = 0.753$ ) PH and temperature ( $r = 0.807$ ), TDS and temperature ( $r = 0.734$ ). Moderately positive correlation exists between the following:

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

| Element  | Zn          | Pb           | Co          | Cu          | Cr          | Mn   | Cd           | V           | Fe          | Ni    | As          | Sb  | Al    | EC          | pH          | TDS         | Temp |
|--|-------------|--------------|-------------|-------------|-------------|--|--------------|-------------|-------------|-------|-------------|---|-------|-------------|-------------|-------------|------|
| Zn   | 1           |              |             |             |             |  |              |             |             |       |             |   |       |             |             |             |      |
| Pb   | 0.01        | 1            |             |             |             |  |              |             |             |       |             |   |       |             |             |             |      |
| Co   | -0.06       | -0.14        | 1           |             |             |  |              |             |             |       |             |   |       |             |             |             |      |
| Cu   | -0.06       | 0.47         | 0.17        | 1           |             |  |              |             |             |       |             |   |       |             |             |             |      |
| Cr   | 0.32        | -0.47        | 0.17        | 0.14        | 1           |  |              |             |             |       |             |   |       |             |             |             |      |
| Mn   | -0.01       | 0.19         | <b>0.62</b> | 0.44        | 0.41        | 1  |              |             |             |       |             |   |       |             |             |             |      |
| Cd   | <b>0.52</b> | <b>0.56</b>  | -0.02       | 0.13        | -0.30       | 0.05   | 1            |             |             |       |             |   |       |             |             |             |      |
| V  | 0.30        | <b>-0.64</b> | -0.15       | -0.02       | <b>0.78</b> | 0.06   | -0.32        | 1           |             |       |             |   |       |             |             |             |      |
| Fe   | -0.36       | -0.11        | -0.07       | <b>0.84</b> | -0.24       | -0.07  | 0.00         | 0.09        | 1           |       |             |   |       |             |             |             |      |
| Ni   | 0.28        | 0.31         | 0.15        | 0.13        | 0.16        | 0.36   | <b>0.60</b>  | -0.26       | 0.00        | 1     |             |   |       |             |             |             |      |
| As   | 0.40        | <b>-0.57</b> | -0.19       | 0.08        | <b>0.65</b> | -0.05  | 0.02         | <b>0.82</b> | 0.47        | 0.04  | 1           |   |       |             |             |             |      |
| Sb   | 0.15        | 0.46         | -0.11       | 0.40        | -0.42       | 0.24   | <b>0.53</b>  | -0.26       | <b>0.82</b> | 0.20  | -0.10       | 1   |       |             |             |             |      |
| Al   | <b>0.64</b> | 0.49         | 0.04        | 0.32        | -0.25       | -0.01  | <b>0.93</b>  | -0.28       | 0.21        | 0.47  | 0.08        | 0.52  | 1     |             |             |             |      |
| EC   | 0.08        | <b>-0.80</b> | -0.18       | -0.28       | 0.47        | -0.17  | -0.46        | <b>0.87</b> | 0.17        | -0.51 | <b>0.75</b> | -0.27   | -0.40 | 1           |             |             |      |
| pH   | 0.36        | <b>-0.86</b> | 0.34        | -0.31       | <b>0.64</b> | 0.16   | -0.21        | <b>0.72</b> | 0.00        | -0.08 | <b>0.68</b> | -0.26   | -0.17 | <b>0.74</b> | 1           |             |      |
| TDS  | 0.08        | <b>-0.80</b> | -0.18       | -0.28       | 0.47        | -0.17  | -0.46        | <b>0.87</b> | 0.17        | -0.51 | <b>0.75</b> | -0.27   | -0.40 | <b>1.00</b> | <b>0.74</b> | 1           |      |
| Temp   | 0.06        | <b>-0.91</b> | 0.20        | -0.16       | <b>0.58</b> | -0.12  | <b>-0.55</b> | <b>0.72</b> | 0.29        | -0.33 | <b>0.58</b> | -0.39   | -0.38 | <b>0.73</b> | <b>0.81</b> | <b>0.73</b> | 1    |
| <b><math>r</math> values <math>&gt; 0.5</math> or <math>&lt; -0.5</math> are significant</b> |             |              |             |             |             | <b><math>r &gt; 0.72</math> Strong correlation</b> |              |             |             |       |             | <b><math>r &gt; 0.80</math> Very strong correlation</b> |       |             |             |             |      |

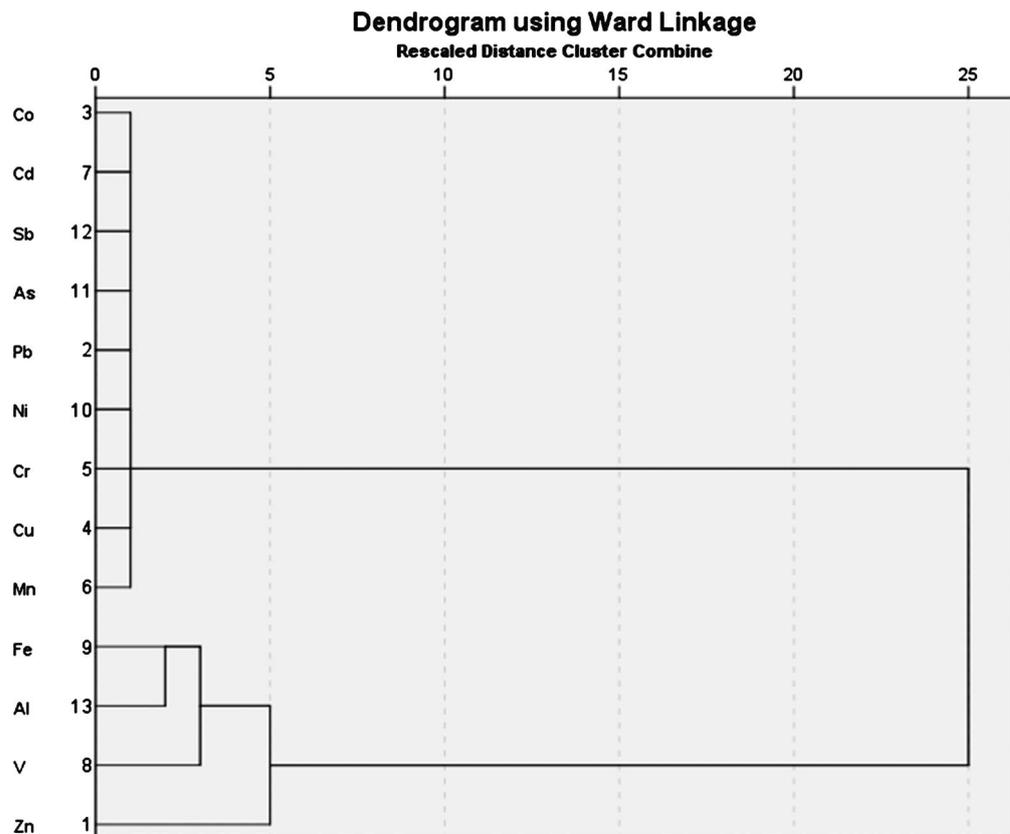
Zn and Al ( $r = 0.642$ ), Co and Mn ( $r = 0.615$ ), Cr and As ( $r = 0.648$ ), Cr and PH ( $r = 0.638$ ), Cd and Ni ( $r = 0.604$ ), As and PH ( $r = 0.677$ ) and Very strong negative correlation exist between Pb and EC ( $r = -0.8$ ), Pb and PH ( $r = -0.859$ ), Pb and TDS ( $r = 0.8$ ), Pb and temperature ( $r = -0.906$ ). A moderately negative correlation exists for Pb and V ( $r = -0.641$ ).

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 [33].

The very strong negative correlation between Pb and pH is an indication that Pb concentrations increase with decreasing pH, as such Pb, has a strong negative correlation with TDS and EC [34]. This is similar to the correlation between Al and Cd, also Fe and Cu.

### 3.5. Hierarchical Cluster Analysis HCA

The R-mode Cluster Analysis CA performed on the samples produced two clusters based on spatial similarities and dissimilarities: Cluster 1; comprised Co, Cd, Sb, As, Pb, Ni, Cr, Cu and Mn which were less soluble and cluster 2; Fe, Al, V and Zn which were more soluble within the ionic content, pH, EC and temperature range of groundwater and of this region shown in **Figure 3**. The relative



**Figure 3.** Dendrogram of trace metals in groundwater of the study area made up of two clusters: Cluster one (09) elements Co, Cd, Sb, As, Pb, Ni, Cr, Cu, Mn and cluster two; (04) elements; Fe, Al, V, Zn.

elevated concentrations of the cluster two elements (Fe, Al, V and Zn) is due to the ease with which they can be dissolved into solution within the EC, pH and temperature ranges found in the study area [35].

### 3.6. Health Risk Assessment ADD, HQ, CR, HI

Human health risk assessment was done to measure or 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 metals selected, **Table 6**. The sample population was divided according to ten age groups **Table 3**. Due to behavioural and physiological differences. Carcinogenic and non carcinogenic risk were calculated from the ADD.

ADD values ranged as follows;  $3.4 \times 10^{-7}$  to  $7.4 \times 10^{-6}$  (As),  $3.6 \times 10^{-7}$  to  $2.8 \times 10^{-6}$  (Sb),  $1.6 \times 10^{-4}$  to  $3.1 \times 10^{-3}$  (Al),  $7.4 \times 10^{-6}$  to  $6.7 \times 10^{-5}$  (Ni),  $1.8 \times 10^{-7}$  to  $2.9 \times 10^{-5}$  (Cd),  $7.2 \times 10^{-7}$  to  $2.3 \times 10^{-5}$  (Co),  $1.4 \times 10^{-5}$  to  $1.2 \times 10^{-4}$  (Cr),  $3.9 \times 10^{-5}$  to  $4.1 \times 10^{-4}$  (Mn),  $1.7 \times 10^{-4}$  to  $4.2 \times 10^{-3}$  (Zn),  $3.6 \times 10^{-6}$  to  $4.5 \times 10^{-5}$  (Pb),  $1.5 \times 10^{-5}$  to  $1.3 \times 10^{-4}$  (Cu),  $3.4 \times 10^{-5}$  to  $5.1 \times 10^{-4}$  (V),  $7.9 \times 10^{-5}$  to  $8.6 \times 10^{-4}$  (Fe) as seen in **Figure 4**.

HQ values ranged as follow;  $2.8 \times 10^{-3}$  to  $2.5 \times 10^{-2}$  (As),  $8.9 \times 10^{-7}$  to  $7.2 \times 10^{-6}$  (Sb),  $2.3 \times 10^{-5}$  to  $4.3 \times 10^{-4}$  (Al),  $3.7 \times 10^{-4}$  to  $3.3 \times 10^{-3}$  (Ni),  $3.7 \times 10^{-4}$  to  $5.8 \times 10^{-2}$  (Cd),  $3.6 \times 10^{-5}$  to  $1.1 \times 10^{-3}$  (Co),  $4.6 \times 10^{-3}$  to  $3.9 \times 10^{-2}$  (Cr),  $6.4 \times 10^{-6}$  to  $2.9 \times 10^{-3}$  (Mn),  $1.5 \times 10^{-4}$  to  $1.4 \times 10^{-2}$  (Zn),  $6.7 \times 10^{-4}$  to  $1.2 \times 10^{-2}$  (Pb),  $2.9 \times 10^{-3}$  to  $2.5 \times 10^{-2}$  (Cu),  $8.9 \times 10^{-2}$  to 0.5 (V),  $1.1 \times 10^{-4}$  to  $1.2 \times 10^{-3}$  (Fe) as shown in **Figure 5**.

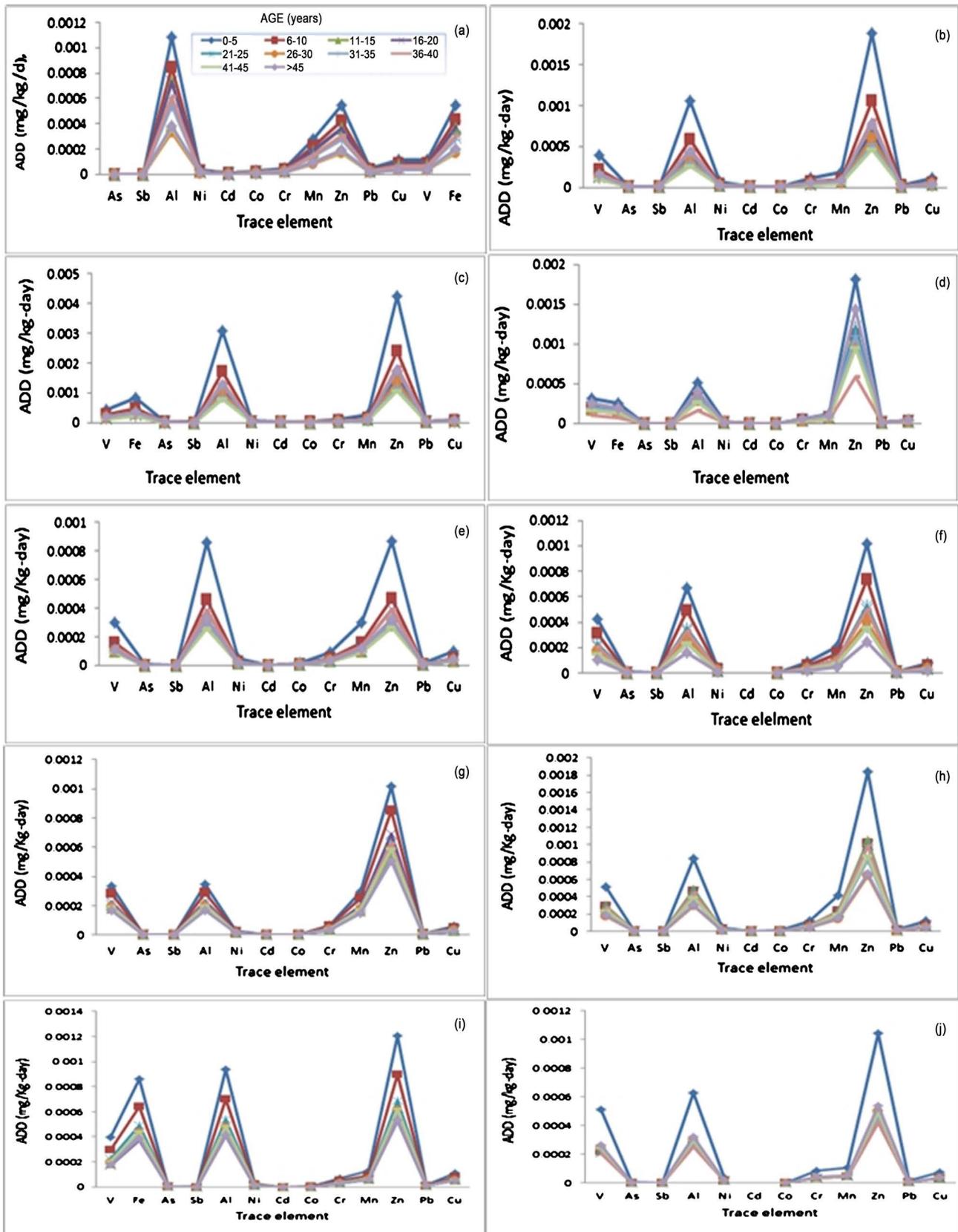
CR for the carcinogenic elements; Pb, Cr, Cd, Ni and As are; (Pb)  $1.4 \times 10^{-8}$  to  $6.7 \times 10^{-6}$ , (Cr)  $2.9 \times 10^{-6}$  to  $2.5 \times 10^{-5}$ , (Cd)  $3.0 \times 10^{-8}$  to  $1.7 \times 10^{-6}$ , (Ni)  $2.3 \times 10^{-6}$  to  $4.9 \times 10^{-5}$ , (As)  $5.1 \times 10^{-7}$  to  $1.1 \times 10^{-5}$  shown in **Figure 6**.

HI is the cumulative sum of HQ. The values ranged between 0.1 and 0.6 for each of the ten (10) age groups indicating no toxicity as in **Figure 7**.

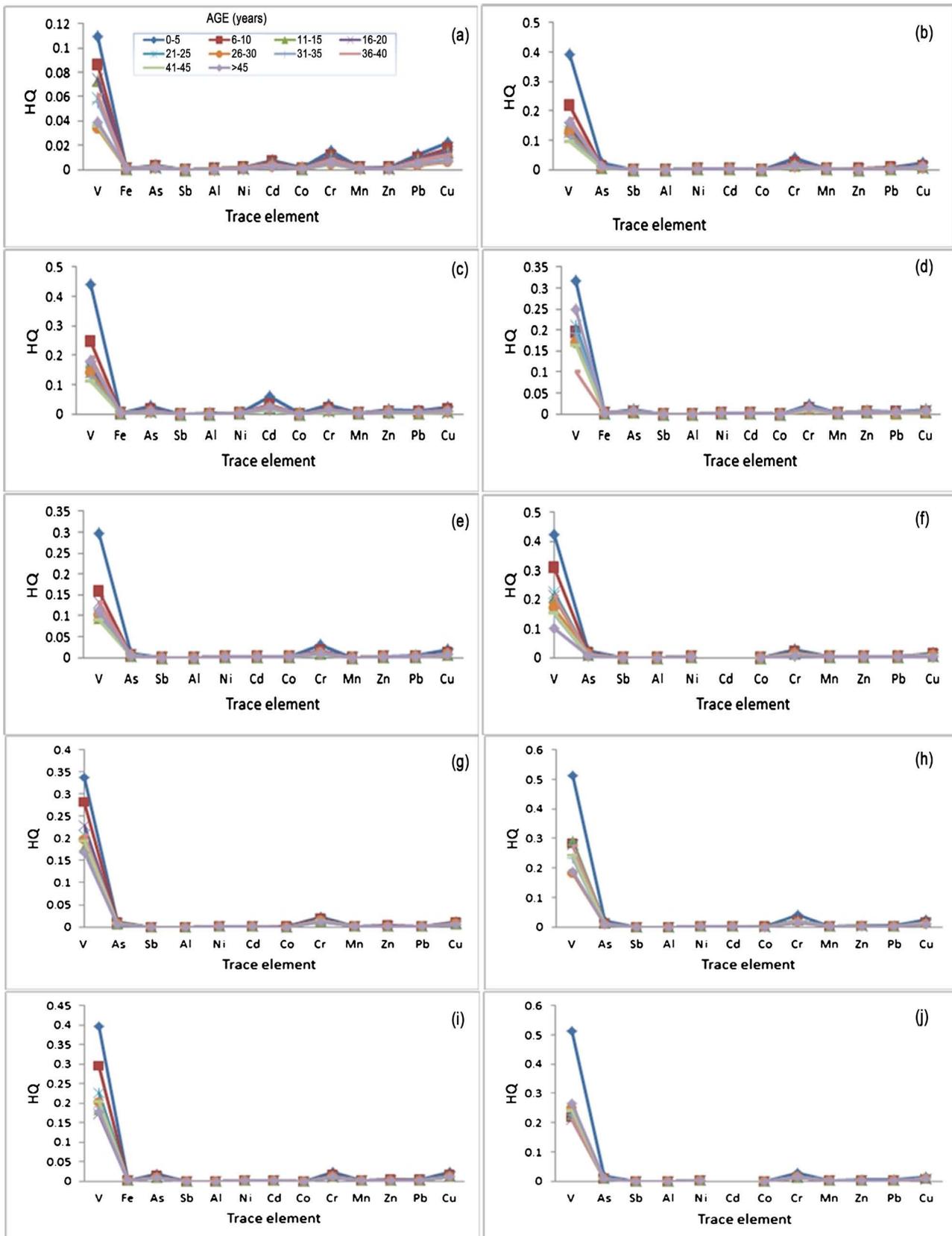
The 0 - 5 years age range had the most elevated ADD values followed by 6 - 10 year age range, consequently the HQ, HI and CR values were relatively higher for these age ranges but were well below 1 indicating an acceptable level and the exposed population is unlikely to experience adverse health effects. This is due to a higher water intake to body weight ratio which would imply a higher risk for children 0 - 10 years old to trace metal cumulative contamination; In Tole for

**Table 7.** Parameters used for estimating exposure assessment [24].

| 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           | <b>Table 3</b> |
| Ingestion rate            | IR     | L/day        | <b>Table 3</b> |
| Contaminant concentration | C      | ug/L         | <b>Table 4</b> |



**Figure 4.** Average Daily Dose (ADD) of each contaminant for each of the ten (10) age groups water intake. All values are below toxic level.



**Figure 5.** Non-carcinogenic hazards; hazard quotient (HQ) of each contaminant for each of the ten (10) age groups through water intake. All values are below toxic levels.

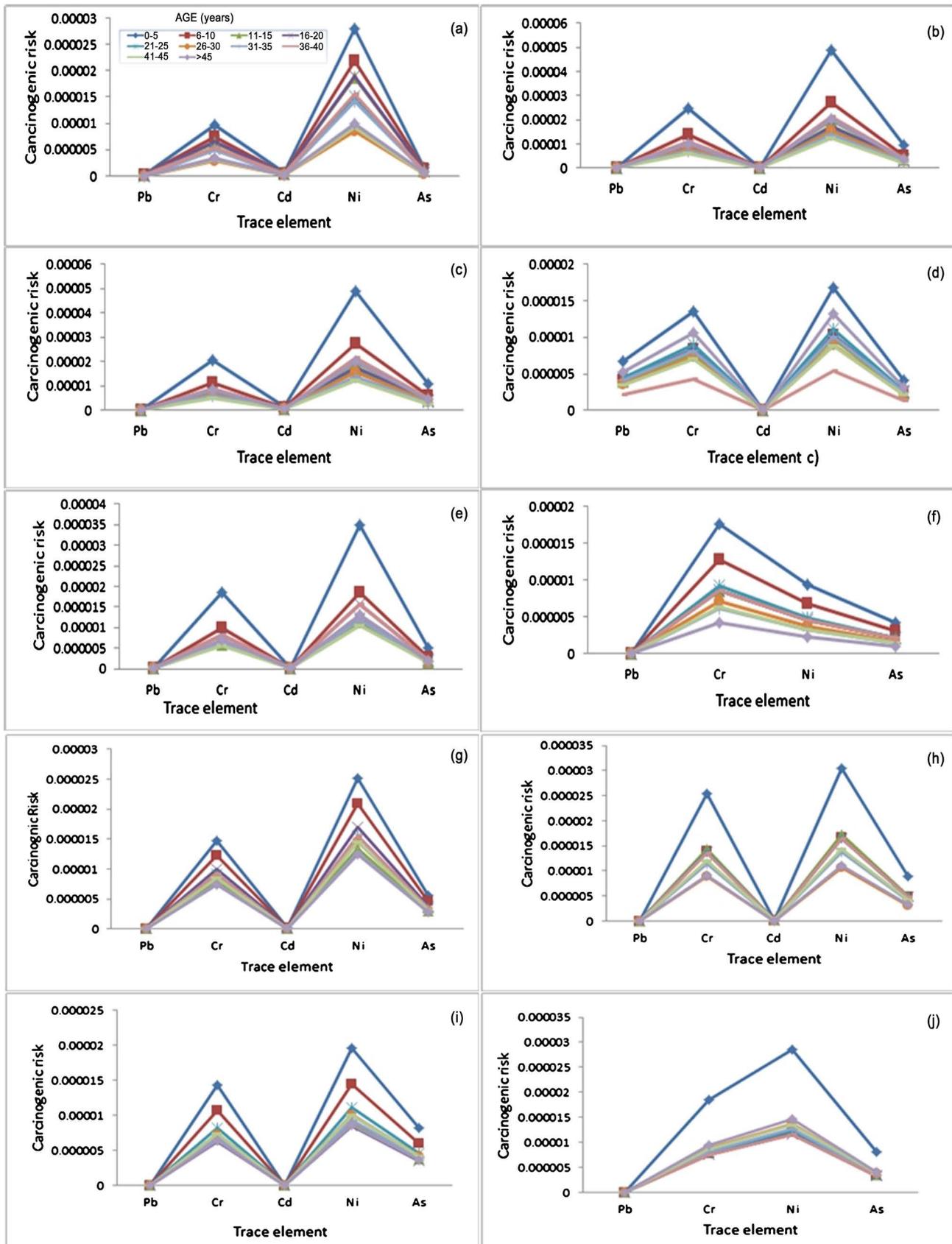


Figure 6. Carcinogenic risk (CR) of each contaminant for each of the ten (10) age groups water. All values are below toxic levels.



**Figure 7.** Non carcinogenic toxic risk index or hazard index (HI) of each contaminant for each of the ten (10) age groups water intake. All values are below toxic levels.

example, the maximum weight of infants 0 - 5 years was 12 kg, of adults 41 - 45 was 82 kg while their water intake max was 2.0 and 5.0 litres respectively. Giving an intake body weight ratio of 2/12 (24%) for infants and 5/82 (4.1%) for adults respectively, a (24/4.1) six times higher trace metal intake cumulative contamination ratio for this two groups in Tole.

Pb and Cd values were less than  $1 \times 10^{-6}$  and are not regarded as to cause significant health effects. 82.5% of Cr values are regarded as not to cause significant health effects and 17.5% regarded generally as in the satisfactory range. 21% of Ni values are regarded as not to cause significant health effects 79% are regarded generally as satisfactory range. For As, 99% of values are not regarded as significant to cause health effects and 1% regarded as satisfactory presented in **Table 8**.

Increased water demand due to unprecedented population growth and urbanization has led to serious water supply crisis within the Piedmont Regions of Mount Cameroon. This has compelled many inhabitants to rely mostly on springs as sources for drinking water. To ascertain the suitability of these alternative groundwater sources for human consumption, an assessment of the heavy metal content was requisite.

#### 4. Conclusions

The trace metal concentrations in this region are low. There low trace metal concentrations have been attributed to the geology; absence of rocks containing high concentrations of trace metals, the slightly acidic to neutral pH, low temperatures  $< 25^{\circ}\text{C}$  and the short residence time of ground water, conditions necessary for trace metal oxidation, dissolution and precipitation in groundwater.

Although other studies around Mt. Cameroon postulated anomalous concentrations of arsenic in water on the plains of the leeward side of Mount Cameroon [2] and another determined high concentrations in the soils [3] on the windward side of Mt. Cameroon respectively, this study has found no anomalous concentration of any trace metal in the groundwater.

Health risk assessment ADD, CR, HQ and HI of the groundwater sources in this area were within the standard permissible limits indicating an acceptable level.

**Table 8.** Classification of health risk assessment carcinogenic and non-carcinogenic risk).

| INDEX | Range                | Classification                      | (%)  | Source |
|-------|----------------------|-------------------------------------|------|--------|
|       | $<10^{-6}$           | cause no significant health effects | 82.5 |        |
| CR    | $>10^{-6} - 10^{-4}$ | Generally satisfactory              | 17.5 | [36]   |
|       | $>10^{-4}$           | Intolerable                         | NA   |        |
| HQ    | $<1$                 | Acceptable level (no concern)       | 100  | [24]   |
|       | $>1$                 | No carcinogenic adverse effects     | NA   |        |
| HI    | $<1$                 | Safe                                | 100  | [24]   |
|       | $>1$                 | Unsafe                              | NA   |        |

The exposed population is therefore unlikely to experience immediate adverse health effects from consuming groundwater in the Piedmont region of Mt. Cameroon.

However, monitoring is recommended due to the rapid increase in population and activities of agro-industrial complexes in this region that are using various fertilizers and insecticides.

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## Submission Declaration and Verification

The submission of this article implies that the work described here-in has not been published previously and that it is not under consideration for publication elsewhere; that this publication has been approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out, and that, if accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright holder.

## Highlights

- Trace elements in groundwater of a volcanic terrain;
- Health Risk assessment;
- Water resources evaluation;
- Groundwater Physico-chemical quality;
- Piedmont regions of Mount Cameroon-Africa.

## Conflicts of Interest

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

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