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Behavior of major ions and heavy metals risk assessment in spring and surface water on the southwest slope of Mount Cameroon (Western Africa)

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The coastal flanks of Mt Etinde is wedged between the sea and the southwestern slope of Mt Cameroon. The only fresh water resources available for multipurpose uses in this area are mountain springs and streams that drain volcanic materials. To access the sources, processes and assess the ecological risk associated with hydrochemicals and heavy metals in these mountain water resources, 18 water samples were collected in different seasons at 4 locations between May 2009 and December 2010 for major ions and heavy metals determination. The sampled waters ranged from neutral to slightly alkaline, weakly mineralized and dominated by Ca–Mg–HCO₃ water type irrespective of season. The hydrochemical ratios revealed ions chemistry mostly influenced by geogenic source of silicate rock weathering and atmospheric inputs. Sampled waters had low concentration of heavy metals which are less mobile in the aqueous phase, controlled by hydraulic condition. Geochemical processes of mineral dissolution and reverse ion exchange coupled with hydrodynamic processes of flushing at the weathering front and soil leaching are the main controls on the water chemistry in the area. Despite agricultural and other anthropogenic activities, quality indices in the study area indicate the absence of anthropogenic inputs.

Key words: Major ions, heavy metals, rocks weathering, soil leaching, water quality assessment.

INTRODUCTION

The determination of major and trace elements in surface and groundwater is necessary to ascertain geochemical profiles that differentiate natural and human influences on water chemistry. Rock weathering, anthropogenic and atmospheric inputs are the most important processes controlling the water quality. The natural hydrogeochemical
characteristics of spring and stream water in a given region is the reflection of the chemical composition of minerals of rocks, as well as the physico-chemical process of chemical weathering and erosion, which cause mineral dissolution (Braun et al., 2005; Nkoue et al., 2021). Depending on the nature of the dissolved minerals, the chemical composition of surface and groundwater may be enriched with metals, metalloids or ions involved in geochemical processes such as sorption, redox reactions, ion exchange, and complexation, which may control its hydrogeochemistry and subsequently affect the water quality (Ako et al., 2012; Asare-Donkor et al., 2018). Hydrogeochemical characterisation can be understood via several methods, among which, the typical hydrogeochemical ratios, which can evaluate the origin and processes of water resources and the factors that influence the water chemistry (Zhu et al., 2007).

In recent years, there has been an increasing interest in heavy metal contamination and toxicity in aquatic systems (N’guessan et al., 2009; Yi et al., 2011; Li et al., 2014; Khan et al., 2013; Asare-Donkor et al., 2018; Ibanga et al., 2018; Raafat, 2020; Sharmin et al., 2020). A number of studies have found that spring and stream water may contain elements such as arsenic, cadmium, chromium, lead, selenium, and mercury for which contamination is a major environmental concern due to their toxicity, carcinogenicity, and mutagenicity even at low concentration (Moore et al., 2011; Ifegwu and Anyakora, 2012; Mandeng et al., 2019). Heavy metals in rivers could be related to agricultural and industrial waste and by-products (Naveedullah et al., 2013; Zhou et al., 2020), significant inputs may result from geogenic-lithogenic sources from rock weathering, volcanic activities and geothermal processes (Serelis et al., 2010; Ali et al., 2019).

Rivers which receive volcanic inputs and/or hydrothermal hot springs at flanks of the volcanoes may be heavily affected. Viviroli et al. (2020) highlighted the importance of mountain water resources at global scale and the dependence of lowland inhabitants on these resources, which often deliver high runoff to the subadjacent lowlands used for irrigation, industry, drinking and domestic purposes. Evaluation of the quality of water at flanks of the volcanoes is essential since these waters could be rich in elements owing to the rock-water interaction (Durowoju et al., 2019). The situation calls for concern in the coastal slope of Mt Cameroon where spring water and torrential runoff at flanks are the only freshwater resources available for drinking and other uses especially in the localities of Batoke, Etinde and Bakingili. Indeed, because of its high touristic attraction and fertile soils, this area is experiencing fast growing population and strong agricultural developments which has not been matched by the provision of basic service infrastructure for potable water supply and sanitation. Several studies dealing with water quality problems have been done in the Mt Cameroun area (Endeley et al., 2001; Riotte et al., 2003; Benedetti et al., 2003; Ako et al., 2012). However, there is still little known about the assessment of water resources in relation to heavy metals, particularly in the area of Mt Etinde where water-rock interaction and hydrothermalism could contribute heavy metals supply in groundwater and control the spring and stream water chemistry. Because water quality is mainly concerned with the combined effects of heavy metals, measuring the concentration of heavy metals and determining the multi-element indices (heavy metal pollution index (HPI), Heavy metal evaluation (HEI), contamination factor (Cd) and modified contamination factor (mCd)... is essential in monitoring water quality (Vu et al., 2017; Ghaderpoori et al., 2018).

The coastal slope of Mt Cameroon is an ideal target to conduct hydrochemical assessment of heavy metals in view of sustainable management and protection of freshwater resources. This humid tropical area is characterized by extreme rainfalls and elevated temperatures all year long, which enhances intense weathering conditions and soil erosion, promoting the release of hydrochemicals and heavy metals in outflowing waters from torrential runoff and springs of the flanks of Mt Etinde volcano (1713 m a.s.l). This justifies the long monitoring that has been initiated in the framework of this study, in order to characterize the water chemistry, ascertain the sources and processes of ions and heavy metal concentrations to assess the water quality status.

MATERIALS AND METHODS

Study area

The study area is a coastal strip at the foot of the of Mt Etinde (1713 m a.s.l) between Batoke and Bakingili, located on the slope of the SW oceanic border of Mt Cameroon Volcano (4100 m a.s.l). It lies between latitude 4°1’and 4°7’N and longitude 9°1’and 9°9’E (Figure 1). The climate is tropical humid type with two distinct seasons: a dry season from November to April and a wet season from Mai to October (Olivry, 1986). Normal annual rainfall varies from about 5000 to 9000 mm (Etame et al., 2009b). The mean annual temperature is 26°C. The vegetation changes with altitude from a dense semi-deciduous forest at the base of Mount Etinde (<800 m asl) to a less dense mountain forest towards the summit (Letouzey, 1985; Thomas and Cheek, 1992; Tchouto, 1996).

Geology and geomorphology

Mt Etinde is a volcano, belonging to the volcanic Line of Cameroon (Central Africa). Lava flows of Mt Etinde are dated at from 1.1 Ma (Fitton, 1987) to 0.65 Ma (Nkoumbou et al., 1995). Geologically, it is
composed under-saturated series in silica mainly composed of layered nephelinitic tuffs, nephelinites, nephelinites to hauyne melilite or garnet-red, leucito-nephelinites to aenigmatite and haunophyres (Mouafo, 1988; Nkoumbou et al., 1995; Benedetti et al., 2003; Etame et al., 2009a; Rospabé, 2014), which do not seem comagmatiques with alkali basalts of Mt Cameroon.

Soils on the flanks of Mt Etinde are weathered haplic cambisoil, typical of most mountainous humid equatorial climatic zones. Such weathered soils are high in clay content and residual elements such as Fe, Al, and Si and low in alkali metals and alkaline earth metals (Etame et al., 2009a). These cambisols are less than 2 m thick in the slopes and are derived from in-situ weathering of underlain nephelinitic parent rocks (Etame et al., 2009a,b). The slopes of Mt Etinde have deeply incised V-shape valleys separating sharp crests. These valleys commonly have seasonal streams that run dry in the dry season.

Hydrology and hydrogeology

The study area is located in the moist tropics close to the equator where annual rainfall exceeds evapotranspiration. This southwestern atlantic border of Cameroon is the rainiest in the country and among the wettest regions in the world (Olivry, 1986), with an average precipitation of about 8000 mm/year. About 90% of annual precipitation falls during May–October, followed by a dry season from November to April. This seasonality is illustrated in Figure 2, which shows the rainfall record for the period between 2003 and 2013 at the monitoring station of Issongo that the Cameroon Development Coorporation (CDC) maintains on the west slope of the Mt Cameroon at 3 km from Mt Etinde. Precipitation peaks during July-August when the Intertropical Convergence Zone (ITCZ) is passing across the region, with little rain falling during the dry season between December and February. Orographic enhancement of precipitation by the Mt Cameroon is pronounced, with the western slope receiving approximately 70% of annual rainfall in the region. The hydrographic network of Mount Etinde is characterized by streams that flow through the various “V” shaped surrounding the massif. The runoff in this area is observed to be dominated by torrential streams that springs on the flanks of the mountain. Runoff from storm events tend to rise and decay very rapidly consequently, streams are seasonal at high altitudes, while at low altitudes they are permanent. Nephelinitic lavas surrounding the Mt Etinde cone are generally fractured forming the potential aquifers. High precipitation and fracturing supported by steep slope cause most of the springs to emerge on this formation particularly in the flanks of the mountain. In fact, in the dry season, high-altitude rivers acquire a buried regime due to low hydraulic gradient (Nkoumbou, 1990).

Sampling and laboratory analysis

The sampling points were selected based on their accessibility and their use by the population (Fig. 1). Surface waters were sampled at tree points (ET1, ET2 and ET3) representing the outlets of torrential streams. Spring water was sampled at a single point at the foot of the Mt Etinde at Bakingili (BA), used for drinking purpose. The characteristics of these points are presented in Table 1.
The sampling bottles (polyethylene bottles and glass vials) were pre-washed with ultrapure nitric acid at 15 N and rinsed repeatedly with deionized water, then oven dried and stored in plastic bags until sampling. The samples were taken on different dates in the dry and wet season. Total number of 18 samples were collected in 0.5 L polyethylene bottles for the analysis of major ions and physicochemical parameters and total number of 9 samples were collected for heavy metals in 0.60 ml glass bottles. The syringe filters were rinsed with the sampling water before the collection of water samples. Each bottle was rinsed three times with the sampling water before the collection of water samples. 2 drops of nitric acid were added to each sample for heavy metals analysis. All the samples thus collected were stored in a cooler until the transport to the laboratory.

pH was measured by a precision WTW-PH 330i/SET probe, while conductivity was determined using a precision WTW-LF 325-B/SET probe. Alkalinity was determined by headline volumetric titration with hydrochloric acid using Grant method, with an analytical error of <3%. Major anions were determined by ion chromatography, High Performance Liquid Chromatography (HPLC - Dionex ICS-90) with a precision of ±2% at the Laboratory of Water Analysis (LAGE), Cameroon Institute of Geological and Mining Research (IRGM). Major cations and heavy metals were determined by ICP-MS, at the laboratory of « IRD-CEREGE, Institut de Minéralogie et Physique des Milieux Condensés, Paris, France ». The accuracy of the method was assessed by the analysis of reference materials (SLRS4) with deviation of < 0.07%.

Heavy metal indices calculations

Heavy Metal Pollution Index (HPI) was proposed by Mohan et al. (1996). It is an index which allows to assess the overall water quality with regard to heavy metals. It is determined by Equation 1.

\[
HPI = \frac{\sum_{i=1}^{n} WiQ_i}{\sum_{i=1}^{n} Wi}
\]

Where \(n\) is the number of samples considered, \(Wi\) is the inverse of the standard value \((Si)\) of the \(i^{th}\) metallic element, \(Q_i\) is the sub-index of the \(i^{th}\) metallic element. \(Q_i\) is determined by Equation 2.

\[
Q_i = \frac{\sum_{i=1}^{n} |Mi - II|}{Si - II} \times 100
\]

Where \(Mi\) is the average concentration of element \(i\) in a given sample, \(II\) is the maximum ideal concentration for element \(i\).

The HEI method like the HPI gives an overall quality of the water with respect to heavy metals (Edet and Offiong, 2002). The HEI is computed as:

\[
HEI = \frac{\sum_{i=1}^{n} C_i}{MAC}
\]

where \(C_i\) is the monitored value of the \(i^{th}\) parameter and \(MAC\) the maximum permissible concentration of the \(i^{th}\) metal parameter.

Contamination degree of heavy metals was calculated using the formula prescribed by Hakanson (1980):

\[
C_d = \sum_{i=1}^{n} \frac{C_f}{\sum_{i=1}^{n} C_f}
\]
hydrochemical characteristics

Table 2 presents the physicochemical parameters and the summary descriptive statistics of the major ions in the water samples (mg/L) of the studied area. Concentrations of hydrochemical constituents are illustrated in box plots (Figure 3). Most parameters occur in narrow ranges with little standard deviations (SD), indicating chemical composition affected by homogenous processes and single source. pH values ranged between 7.03 and 9.03 with a mean of 7.76±0.53, indicating that the surface waters are neutral to slightly alkaline. In general, pH values were within the range of the WHO (6.5-8.5) limits for drinking water, except a single sample (11/06/2009 at ET1). Electrical Conductivity (EC) ranges between 50.9 and 89.6 µS/cm with an average value of 74.94±12.05 µS/cm, which indicates that water is weakly mineralized. Lowest EC and pH were recorded near the peak of the precipitation, indicating dilution process by weakly acidic and low mineralized meteoric waters. Akalinity ranged between 278 and 832 µeq/L with a mean value of 623±180 µeq/L. Total suspended sediments (TSS) was between 2.2 and 18.2 mg/L, averaging 6.38±5.17 mg/L.

In all the water samples, the total cation charge (TZ = Na⁺ + K⁺ + 2Mg²⁺ + 2Ca²⁺) imbalanced the total anion charge (TZ = Cl⁻ + 2SO₄²⁻ + 2CO₃²⁻ + HCO₃⁻). For the normalized inorganic charge balance (NICB = (TZ⁺ - TZ⁻)/TZ⁺), all samples had an NICB < -70%, reflecting a cationic deficit, mainly due to the abundance of bicarbonates. Major ion concentrations were low (Table 2) and were in the order of HCO₃⁻ >> NO₃⁻ >> Cl⁻ ≈ SO₄²⁻ > PO₄³⁻ > F⁻ for major anions. HCO₃⁻ ranged from 16.96 to 50.75 mg/L and accounted for more than 92% of the TZ. Nitrate varied from 0.00 and 1.98 mg/L with an average value of 0.89 mg/L. Chlorine ranged from 0.69 to 1.97 mg/L and sulfate ranged from 0.47 to 1.28 mg/L with an average of 0.88 mg/L. Phosphorus had the lowest concentration, ranges between 0.00 and 0.27 mg/L with averages value of 0.07 mg/L. Average cation concentration where in the following order: Ca²⁺ > Mg²⁺ > K⁺ > Na⁺. Ca²⁺ represented on average 31.04% of the TZ⁺. While Na⁺ only accounted for 2.06% of the TZ⁺. The concentration of calcium and magnesium ranged between 3.94-7.94 mg/L and 1.55-6.65 mg/L respectively. Sodium and potassium values ranged respectively from 0.17 to 1.62 mg/L and 0.82 to 4.57 mg/L. The concentrations of cation were found to be slightly higher in spring water (BA) than in streams (Table 2). The levels of ions in all the spring and stream water samples fall below the WHO (2017) maximum acceptable limits. Temporal variations of major ions (Figure 4) showed a slight decrease in concentration towards the period of precipitate peak, which was explained by dilution owing to the heavy rainfall during this period. However, highest nitrate concentrations were observed during this period, which linked the origin of this element to the leaching of the soil. Such seasonal variations is typical of poorly saturated and highly leached milieu in which springs and surface water are diluted during the rainy season (Viers et al., 2000).

**RESULTS AND DISCUSSION**

**Hydrochemical characteristics**

Table 1. Location and description of the sampling points.

| Sampling point name | GPS coordinates          | Types of uses and influences                                                                 |
|--------------------|--------------------------|-----------------------------------------------------------------------------------------------|
| ET1                | 09°46'48"E-04°02'42"N   | It is located in a marshy area in which there are also plantations. The people of this area use the water from this stream, called onkogobong, for drinking. |
| ET2                | 9°05'42"E-04°02'13"N    | It is located below the main road connecting Batoke to Bakingili (South-West). Its water is used by local populations to wash clothes and cars. It is also used as bath water and dishes. |
| ET3                | 09°05'45"E-04°01'59"N   | It is located in the city of Batoke. The populations use it as water for the dishes, the linen but also the bath. |
| BA                 | 09°02'6″-04°04'05″N      | It is located near the station of Bakingili and is used for drinking, laundry, dishes and bathing. |

Where $C_a$ is the contamination degree, and $C_i$ the contamination factor, $n$ the number of analysed elements. The contamination factor is expressed as follows:

$$C_f = \frac{C_i}{C_n} \tag{5}$$

Where $C_i$ is the contamination factor of the $i^{th}$ parameter, $C_i$ is the monitored value of the $i^{th}$ parameter, and $C_n$ is the standard value of the $i^{th}$ parameter.
Major anions and cations data obtained for the spring and stream water samples were plotted on the Piper trilinear diagram (Piper, 1944) to classify the water according to the hydrochemical facies. The relative abundance of the anions and cations are shown in Figure 5. The plot reveals a single type of water, predominantly influenced by the Ca-Mg-HCO₃ hydrochemical facies. This facies remains the same at all sampling point whatever
Figure 3. Box plots illustration of the hydrochemical characteristics of water in the study area.

Figure 4. Temporal variation of major ions in stream water of Mt Etinde.

The period of the year. The combined distribution of both cations and anions showed dominance of alkaline earth (Ca+Mg > Na+K) and weak acids (CO$_3$+HCO$_3$ > Cl + SO$_4$) indicating the temporary hardness of these waters.
Controls processes of major ions in water

By using the chemical components in water and relationships between the ionic species, the sources of the ions and chemical processes that generate them can be determined. These include salt dissolution, seawater intrusion, silicate weathering and ion exchange (Hounslow, 1995; Fisher and Mullican, 1997; Han and Liu, 2004; Diaw et al., 2012).

The Na\(^+\) + K\(^+\) versus Cl\(^-\) + SO\(_4^{2-}\) was plotted (Figure 6A) to determine the origin of these parameter in spring and stream waters. The plot shows samples falling on and below the 1:1 line. This observation suggest mineral dissolution as the process controlling the major ion chemistry. Cl\(^-\) and SO\(_4^{2-}\) accounted for less than 5% of the TZ, which indicates that evaporite dissolution is not a possible source of these ions. This finding is consolidated by the dominance of Ca\(^{2+}\) over SO\(_4^{2-}\) in 100% of the samples (Table 3), confirming that Ca\(^{2+}\) source was other than gypsum dissolution (Hounslow, 1995). Although chloride content exceeding sodium expresses the predominance of marine influence for which the Na\(^+\)/Cl\(^-\) molar ratios is equal to 0.55 (Meybeck, 1987; Stallard and Edmond, 1983), the average Na\(^+\)/Cl\(^-\) molar ratio of 0.57 (Table 2) obtained here could be explained by precipitations of marine origin or fixation of Na\(^+\) in the form of clay minerals (Kolahchi and Jalali, 2006).

In order to ascertain the influences of rock-water interaction, evaporation and precipitation on the water chemistry, we plotted the total dissolved solids (TDS) versus the weight ratio of (Na\(^+\)+K\(^+\))/(Na\(^+\)+K\(^+\)+Ca\(^{2+}\)) and Cl\(^-\)/Cl\(^-\)+HCO\(_3^-\) according to Gibbs (1970). The data points suggest chemical weathering of rock and rainwater supplies as the main factors controlling the water chemistry in this area (Figure 7). This observation is supported by the Cl\(^-\) and K\(^+\)concentrations exceeding Na\(^+\), which confirms the contribution by rainwater resulting from the evaporation of seawater. The low dissolved ions content coupled with nearly neutral to alkaline pH suggest short to average water-rock interaction time. This is further supported by the Gibbs plot with the data points plotted near the rainfall dominance feld. This short water–rock interaction time can be attributed to the fractured nature of the nephelinitic formation on the slope of Mt. Etinde coupled with high hydraulic gradient due to high rainfall. During the dry season, there is a decrease in hydraulic gradient due to low rainfall. This leads to an increase in the water rock interaction time, enhancing alkaline conditions (Makoba and Muzaka, 2019).

The molar ratios of Mg\(^{2+}\)/Ca\(^{2+}\) and Na\(^+\)/Ca\(^{2+}\) have been
Figure 6. The ionic ratio plots for plot (A) Na⁺+ K⁺ versus Cl⁻ + SO₄²⁻, (B) Mg²⁺/Ca²⁺ versus Na⁺/Ca²⁺, (C) Ca²⁺ + Mg²⁺ versus HCO₃⁻ + SO₄²⁻, (D) Na⁺+K⁺ versus T²⁺, (E) (Ca²⁺+Mg²⁺) versus T²⁺, (F) (Na⁺ - Cl⁻) versus (Ca²⁺ + Mg²⁺) – (HCO₃⁻ + SO₄²⁻).

Table 3. Molar ratios of chemical species in surface water.

|      | ET1 | ET2 | ET3 | Mean | Min | Max | Std. |
|------|-----|-----|-----|------|-----|-----|-----|
| Na⁺/Cl⁻ | 0.51 | 0.43 | 0.26 | 0.64 | 0.35 | 0.76 | 0.62 | 0.95 | 0.39 | 0.57 | 0.26 | 0.95 | 0.23 |
| Cl⁻/HCO₃⁻ | 0.04 | 0.05 | 0.09 | 0.03 | 0.07 | 0.06 | 0.03 | 0.03 | 0.03 | 0.03 | 0.03 | 0.09 | 0.02 |
| Ca²⁺/SO₄²⁻ | 30.15 | 21.83 | 19.7 | 25 | 21.76 | 16.46 | 16.6 | 17.7 | 13.5 | 15.13 | 19.78 | 13.5 | 30.15 | 5.05 |
| Mg²⁺/Ca²⁺ | 0.65 | 0.62 | 0.64 | 0.68 | 0.65 | 0.65 | 0.69 | 0.69 | 0.61 | 0.62 | 0.65 | 0.61 | 0.69 | 0.03 |
| Na⁺/Ca²⁺ | 0.77 | 0.76 | 0.73 | 0.83 | 1.03 | 0.87 | 1.13 | 1.01 | 1.18 | 1.01 | 0.932 | 0.73 | 1.18 | 0.16 |
| CAI | -5.4 | -4.5 | -2.4 | -6.8 | -3.6 | -5.3 | -8.4 | -7.1 | -11.3 | -11.8 | -6.66 | -11.8 | -2.4 | 3.10 |

CAI: chloro-alkali index.

used to determine the sources of calcium and magnesium ions in surface water. These molar ratios are distinct in waters draining limestone, dolomite and silicates basement, in which there are respectively about 0.03; 1 and 1 for Mg²⁺/Ca²⁺ and 0.005; 0.01 and 1.73 for Na⁺/Ca²⁺ (Han and Liu, 2004; Mtoni et al., 2013). In this study, all samples had Mg²⁺/Ca²⁺ and Na⁺/Ca²⁺ molar ratios ranging from 0.61 to 0.69 and 0.73 to 1.18, respectively (Table 3). On the plot of Mg²⁺/Ca²⁺ versus Na⁺/Ca²⁺ according to Han and Liu (2004), all water samples fall on the axis between the limestone and silicate poles, getting closer to the silicate pole (Figure 6B). This indicates the dominance effect of silicate minerals with little effect from calcite dissolution. To further determine the likely influence of silicate dissolution, Ca²⁺+Mg²⁺ versus SO₄²⁻+HCO₃⁻ was plotted. Fisher and Mullican (1997) established that a charge balance with a linear slope of 1:1 will exist between the Ca²⁺+Mg²⁺ and SO₄²⁻+HCO₃⁻ if they are derived from basic dissolution of carbonate and evaporate minerals (calcite, dolomite and gypsum). In this study, majority of data plot fall above the equilin 1:1 (Figure 6C).
suggesting a deficiency of alkaline earth elements (Ca$^{2+}$+Mg$^{2+}$) over $\text{SO}_4^{2-}$+$\text{HCO}_3^-$ which reflects additional sources of $\text{HCO}_3^-$ supplied by silicate weathering (Mortatti and Probst, 2003; Wirmvem et al., 2013). However, some few samples from the rainy season were plotted along the equiline 1:1. This could illustrate the dissolution of calcite mineral that was found associated to phillipsite in this area (Etame et al., 2009b). The plot of Na$^+$+K$^+$ versus TZ$^+$ (Figure 6D) shows all points far below 1:1 line with a strong positive correlation ($R^2=0.8$), indicating a higher ratio of alkaline cations from silicate weathering relative to saline cations (Stallard and Edmond, 1983; Srinivasamoorthy et al., 2014). Furthermore, the plot of (Ca$^{2+}$+Mg$^{2+}$) versus TZ$^+$ (Figure 6E) fall on and below the line 1:1 with very strong positive correlation ($R^2=0.98$), reflecting an increasing contribution of Na$^+$ and K$^+$ as TDS increases. This confirms that Na$^+$ and K$^+$ are almost exclusively from silicate weathering.

Previous geochemical studies (Nkoumbou et al., 1995; Etame et al., 2009a,b) revealed that the main primary mineral assemblage in the study area are dominated by Clinopyroxene, feldspathoids and phillipsite. Etame et al. (2009a) showed that the weathering process of these minerals, which involves the release of $\text{HCO}_3^-$ in the water, leads to the formation of halloysite, hematite and gibbsite. Although the presence of these secondary minerals in the soil rather reflects congruent weathering, the significance of cation-exchange in controlling ionic concentrations in solution was tested. The relationship between Na$^+$ and Cl$^-$ (representing the amount of Na$^+$ gained or lost compared to that provided by salt dissolution) and (Ca$^{2+}$ + Mg$^{2+}$) - (HCO$_3^-$ + $\text{SO}_4^{2-}$) was plotted (Figure 6F). The latter represents the amount of Ca$^{2+}$ and Mg$^{2+}$ gained relative to that provided by carbonate or sulphate mineral dissolution. If ion exchange is a significant process in the surface water, the relationship between these variables should be linear with a slope of -1.1 (Fisher and Mullican 1997). In this study, 90% of sample fall below the -1:1 line, showing decreases of (Ca$^{2+}$ + Mg$^{2+}$) - (HCO$_3^-$ + $\text{SO}_4^{2-}$) without any increase of Na$^+$ + Cl$^-$, thus indicating that ion exchange was not dominant, but played a significant role in controlling the ionic content of the surface water. This finding is confirm by the ratio between (Ca$^{2+}$ + Mg$^{2+}$) versus (HCO$_3^-$ + $\text{SO}_4^{2-}$) of figure 6C, in which the majority of the samples fall left to the 1:1 line highlighting ion exchange process in this area (Fisher and Mullican, 1997). Chloro-alkali indices (CAI) also known as an index of base exchange were used to determine the nature of ion exchange in water system. Positive indices indicate the exchange of Na$^+$ and K$^+$ in water with Ca$^{2+}$ and Mg$^{2+}$ in soil mineral (chloro-alkaline equilibrium), while negative indices depict the reverse situation (chloro-alkaline disequilibrium). In the volcanic area of Etinde, all the water samples gave negative CAI (Table 3) suggesting reverse ion exchange process of Ca$^{2+}$ and Mg$^{2+}$ in water.

![Figure 7](image_url). Gibbs diagrams presenting a simple plot of TDS versus the weight ratio of (Na$^+$+K$^+$/Na$^+$+K$^+$+Ca$^{2+}$) and Cl$^-$/Cl$^-$ +$\text{HCO}_3^-$ in stream waters.
with Na⁺ and K⁺ in soil mineral.

**Heavy metals in water samples**

Concentrations of metals in surface water and spring water are shown in Table 4. The highest metal concentrations between 95.89 to 151.96 µg/L and 43.37 to 143.31 µg/L were observed for Fe and Sr respectively. Al, V, Rb, Ba and Mo have concentrations between 6.34 - 13.18 µg/L, 1.60 - 17.14 µg/L, 5.38-11.38 µg/L, 0.82 - 6.85 µg/L and 0.31 - 3.23 µg/L respectively. Heavy metals ranged between 0.00-2.61 µg/L and showed a decreasing order as follows: Zn>Ni>Mn>Cu>As>Co>U>Pb. Cd was below the detection limit. Heavy metals were all lower than the guideline for drinking water (WHO, 1993) and the standard levels regulated content of the environmental quality standards for surface water (UNCED, 1992; UNECE, 1994). Rb, Sr, and Ba concentration were higher and did not show significant temporal variation while the trend of Al, Mn was irrespective of seasons. Concentrations of Cr, Ni, Cu and Co, in surface water were higher at the beginning of the rainy season in May-Jun and decreased in September with the declining rainfall to further decreases to a minimum in December in the dry season. On the other hand, V, Zn, and As concentration increases with the declining rains (Figure 8). Ni, Zn an Cu showed temporal variation in spring water, with a decreasing trend in concentrations during the dry season. This trends show that the behaviour of these metals in water is mainly related to hydrodynamic processes and may be due to flushing of the metal immobilized at the weathering front. According to Etame et al. (2009a), the accumulation of these metals in soils of the studied area is mainly due to adsorption on secondary minerals (haematite, goethite, halloysite). Leaching of these soils during the
Figure 8. Comparison of heavy metals concentration at different sampling periods (29/05/2010 = beginning of the rainy season; 19/09/2010 = declining of the rainy season; 05/12/2010 = dry season).

The rainy season is the primary source of Cr, Ni, Cu, Co, V, Zn, Pb and As in surface water. Metals are also associated to iron oxy-hydroxide, which are controlled by the precipitation-dissolution process as function of physico-chemical (Eh, pH, adsorption) and hydrodynamic changes (Braun et al., 2005). The neutral to slightly basic pH recorded in this study, which reflects the weathering of basic rock of this area, lead to the precipitation of heavy metals. The pH versus metal load were plotted in the diagram to adapt the classification of water samples in the study.
Figure 9. Ficklin-Caboi diagram shows the groundwater classification based on total heavy metal load vs pH of the study area.

Figure 9 presents the plotted data in the diagram, in which 60% of water samples are classified as near neutral low metal class, while 40% are classified as near neutral extreme low metal class. Thus, it can be inferred that metals present in waters of the Mt Etinde area are comparatively low and less mobile in the aqueous phase. This assertion was further verified by comparing the average dissolved heavy metal with the average pedgeochemical content. The mean heavy metal contents in soil and parent rock was considered based on data from Etame et al. (2009b). As shown in Table 5, the percentage of Cr, Co, Ni, Zn, Cu and Pb was very low in the sampled waters, between $8 \times 10^4$ and $10^{\text{ppm}}$, confirming the very low mobility of these metals due to precipitation in soil and sediments. This process could justify the enrichment of these metals in the soil profile compared to the parent rock and appears to be the main controlling process of heavy metals in this milieu.

**Risk assessment of heavy metals**

The carcinogenic risk assessments were calculated for the average concentration of heavy metals in surface water (ET1, ET2, ET3) and spring water (Ba). Heavy metal pollution index and heavy metal evaluation index (HPI and HEI) represents the composite influence of metals on the overall quality of water. These methods have been widely used in the evaluation of surface water quality (Mohan et al., 1996; Prasad and Bose, 2001; Edet...
Table 5. Comparaison of the mean heavy metals content in soil and water.

| Site                        | Cr   | Co   | Ni   | Zn   | Cu   | Pb  |
|-----------------------------|------|------|------|------|------|-----|
| Parent rock (ppm)           | 13.66| 27.36| 13.14| 197.50| 67.87| 7.90|
| Soil (ppm)                  | 59.20| 52.38| 42.24| 174.80| 177.89| 8.99|
| Water (ppb)                 | 0.38 | 0.04 | 0.44 | 0.64 | 0.34 | 0.02|
| Water/Soil ratio (%)        | 0.00064| 0.00008| 0.00104| 0.00037| 0.00019| 0.00022|

Table 6. Mean HPI of stream waters and spring water.

| Heavy metal | Mean value [µg/L] | Standard permissible value [µg/L] | Highest desirable value [µg/L] [ii] | Unit weightage (Wi) | Mean HPI |
|-------------|-------------------|-----------------------------------|-------------------------------------|---------------------|----------|
| Al          | 6.053             | 200                               | 30                                  | 0.005               |          |
| Cr          | 0.69              | 50                                | 50                                  | 0.02                |          |
| Mn          | 0.33              | 300                               | 100                                 | 0.003333            |          |
| Fe          | 118.42            | 300                               | 200                                 | 0.003333            |          |
| Mo          | 1.28              | 70                                | -                                   | 0.014286            |          |
| Cd          | 0                 | 10                                | 3                                   | 0.1                 |          |
| Ba          | 0.59              | 700                               | -                                   | 0.001428            |          |
| Ni          | 0.383             | 20                                | 20                                  | 0.05                |          |
| Cu          | 0.363             | 1500                              | 50                                  | 0.000667            |          |
| Zn          | 0.59              | 15000                             | 5000                                | 0.000067            |          |

Table 7. HPI, HEI and Cd values at different sampling sites.

| Sampling site | HPI | Mean deviation (%) | Deviation with mean HPI value | HEI | Cd     |
|---------------|-----|--------------------|-------------------------------|-----|--------|
| Etinde        |     |                    |                               |     |        |
| ET1           | 2.37| -10.96             | -0.29                         | 0.66| 0.48   |
| ET2           | 2.29| -13.93             | -0.37                         | 0.66| 0.48   |
| ET3           | 3.34| 25.89              | 0.69                          |     |        |
| Bakingili     |     |                    |                               |     |        |
| Rainy season  | 11.55| 52.83             | 3.99                          | 0.23| 0.16   |
| Dry season    | 3.59 | -52.52             | -3.97                         | 0.09| 0.03   |

and Offiong, 2002; Ghaderpoori et al., 2018). The HPI and HEI for the study area are determined by incorporating the mean concentration values of recorded heavy metals and using the standards (Table 6). The mean HPI resulting from surface water and spring water were 2.66 and 7.56 respectively. The HPI was also calculated separately for each individual sample site and the deviation and deviation percentage of individual HPI values compared to the mean were expressed (Table 7). The result of indices showed that the HPI for all the sampling sites were far below the critical limit of 100 reported by Prasad and Bose (2001). By following the approach of Edet and Offiong (2002), the proposed HEI criteria for the samples are as follows: low HEI < 10 indicates high-quality water; medium HEI = 10-20 indicates medium contamination risk and high HEI > 20 indicates high contamination risk. The mean value of HEI was 0.66±14 for surface water and 0.16±0.1 for spring water. The present level of HEI shows that the water quality falls within the first category of low zone of pollution. The degree of contamination (Cd) was used as reference to estimate the extent of metal pollution (Al-Ami et al., 1987). Cd may be grouped into three categories as follows: low (Cd<1), medium (Cd = 1 - 3) and high.
The mean Cd values were 0.48±0.24 for surface water and 0.095±0.09 for spring water, suggesting high-quality water for drinking with regard to heavy metals. The HPI, HEI and Cd calculated for spring water were slightly low in dry season compared to the rainy season, reflecting the importance of hydrodynamic on the release of metal in the water column. The calculated carcinogenic risk assessments have good stability and indicates a unique and natural source of metals in this area, rather related to the soil-geochemical background than to anthropogenic origin. This study demonstrated 'nil to very low' degree of water contamination with respect to the analyzed heavy metals. Thus, the studied area is not subjected to pollution with regard to heavy metals and hence has low potential for carcinogenic risk.

Conclusion

This paper identified possible sources and processes controlling the mineralization of spring and surface water, quantified the level of heavy metals and assessed the human health risks associated with drinking water resources in the Batoke-Etinde-Bakingili coastal strip. Generally, water from the study area is weakly mineralized, chemical ions and heavy metals being associated to natural pedogeochemical source. Findings revealed that these low concentrations of major ions were typical of poorly saturated and highly leached soil resulting from the weathering of silicate mineral rock. The average values of molar ratios revealed that saline and alkaline ions in this area derived from silicate mineral dissolution and precipitations of marine origin, with little effect of calcite mineral dissolution that was found associated to phillipsite mineral. Ions exchange, although not dominant, was found to play a significant role in controlling the ionic content of the surface water, especially the reverse ion exchange process. Heavy metals in the waters were within the acceptable limits of the WHO. Concentrations of heavy metals in this area are mainly controlled by the flushing of metal at the weathering front and the leaching of soil during the rainy season. Precipitation-dissolution process, heavy metal adsorption on secondary minerals and iron oxy-hydroxides can be pointed as major factors regulating the heavy metals in waters of this area. Based on the WQI, the waters of the study area are classified as excellent. The HPI, HEI and Cd were far below the critical limit, indicating high-quality water for drinking with regard to heavy metals. Since the metal concentrations in the soil are quite high, changes in hydraulic conditions and soil acidity can at times lead to the release of heavy metals from soil and sediments to the water column. This paper is a baseline study and could be expanded to sediment geochemical analysis, redox potential analysis, and their roles in enhancing the release of heavy metals in water. Hence in the future, by collecting more samples across the study area could help for effective monitoring and control plans of heavy metal behaviour.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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