Regional Hydrogeochemical Mapping for Environmental Studies in the Mineralized Lom Basin, East Cameroon: A Pre-industrial Mining Survey

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Abstract: The present study is the first appraisal of regional hydrogeochemical programme for environmental assessment of the mineralized Lom Basin in East Cameroon. Fifty-two streamwater samples were collected and analysed for major cations (Ca²⁺, Mg²⁺, Na⁺, K⁺) and major anions (HCO₃⁻, F⁻, Cl⁻, NO₂⁻, NO₃⁻, Br⁻, PO₄³⁻, SO₄²⁻). Calcium and HCO₃⁻ were the dominant ions. The chemical facies for the surface water were CaHCO₃ and NaHCO₃ types indicating a fresh water source. Major ion geochemistry demonstrated the potential to discriminate between natural and anthropogenic origins. Calcium ion, Mg²⁺, Na⁺, K⁺ and HCO₃⁻ had similar distribution trends reflecting weathering from the parent rocks. Sulphate distribution correlated with the occurrence of sulphide minerals associated with hydrothermal gold mineralization in the area while the distribution patterns of NO₃⁻ and Cl⁻ reflected pollution from domestic activities within the municipality. Overall, the chemistry of stream water in the Lom Basin is mainly controlled by silicate weathering with only minor anthropogenic influence. This study forms an analogue for hydrogeochemical mapping in other mineralized terrains in Cameroon.

Keywords: Hydrogeochemical Survey, Major Ions, Provenance, Lom Basin, Cameroon

1. Introduction

Geochemical mapping is crucial in identifying sources of elements for both mineral exploration and environmental monitoring [1–2]. Hydrogeochemical mapping, an integral part of most regional and local mapping surveys [3–4], is particularly useful in mapping a drainage basin that includes a proposed mine site [5]. The Lom Basin in East Cameroon is heavily mineralized especially in gold owing to its regional geological setting. Also, it has a long artisanal and semi-mechanized mining history and is currently a target for industrialized mining. Consequently, research reporting the rock type, age, and the formation history or the reconnaissance gold investigations in this region are numerous [6–9]. Despite this extensive coverage, there is no available data on the chemical composition of streamwater required to establish quality criteria for water in the area. Surface water assessment is of considerable importance especially in areas where indiscriminate disposal of domestic wastes and informal artisanal mining are practised. Water quality also plays a vital role in promoting the standard of human health.

Water is the principal transport pathway for elements derived from the chemical weathering of mineralized rocks and dissolved ion contents in natural waters are routinely...
used to evaluate the surface water quality [10]. Thus, the chemical composition of streams draining a basin is fundamental for preparing regional geochemical baseline maps. Here, baseline refers to the elemental concentration levels in a medium at a particular period [11–12]. These background levels in surface water can be of natural or anthropogenic origin and distinguishing their sources can be quite challenging. Multivariate statistical procedures have often been used to discriminate between patterns of natural and anthropogenic origin [12]. Hence, it is imperative to take into account the origin of the occurrence and concentrations of the dissolved elements for environmental legislation and regulation [13].

This study presents a regional hydrogeochemical baseline prior to industrial mining in the Lom Basin. Other goals are (a) to distinguish between natural and anthropogenic sources of dissolved ions through a systematic sampling of streamwater draining the catchment, (b) to produce geochemical maps of dissolved ions in the area. These data provide information necessary for setting guidelines and legal standards in the region. Moreover, this study forms a reference for hydrogeochemical mapping in other mineralized areas in Cameroon.

2. Study Area

The Lom Basin consists largely of monotonous, gently undulating hills of altitude between 600 and 1100 m. Such topography has resulted in a well-developed dendritic drainage system. Streams within the study area rise from the hills, flow in a general south-west direction and discharge into the Lom River (Figure 1) which eventually empties into the Atlantic Ocean. The area has a hot and humid equatorial climate characterised by a long dry season from December to April, light wet season from May to June, short dry season between July and October and a heavy rainy season from October to November. The average annual rainfall varies from 1500–2000 mm. High temperatures are recorded between January and February, and the mean temperature is around 24.7°C. Shrubs and herbaceous savanna are the dominant vegetation cover which gives way to an evergreen forest further down south.

![Figure 1. Map of study area showing the location, geology, gold mineralization and sampling points.](image-url)
3. Materials and Methods

3.1. Sampling Methodology and Sample/Data Treatment

Systematic sampling of streamwater was carried out at the peak of the dry season in February 2016, covering the southeastern portion of the Lom Basin (Figure 1). During this survey, abandoned and active mine sites were avoided. Field observations such as potential sources of contamination, land use and upstream lithology were documented.

Representative fifty-two streamwater samples were collected from lower order streams (1st-3rd) during low flow conditions following the procedure outlined in the FOREGS (Forum of European Geological Surveys) Geochemical field mapping manual [18]. A sampling density of 1 sample per 5-10 km was used. The position of each sampling site was marked using a Garmin etrex Global Positioning System. A transparent plastic bucket was filled with streamwater, and the pH, electrical conductivity (EC), total dissolved solids (TDS) and temperature were measured in the field using initially calibrated HI 9811-5 Portable pH/EC/TDS/T meter. The electrodes were rinsed before each measurement with the same water that was sampled and after with distilled water. The meter was calibrated for pH after every 10 measurements using standard solutions from the manufacturer. At the end of each day, alkalinity was measured in the field using the HACH Digital Titrator model 16900. Two separate sample sets were collected at each site; one was filtered through 0.45 µm Millipore membrane filters using 50 ml syringes and stored in previously washed new, narrow-mouth, transparent 50 ml polyethylene bottles. On the same day, 1 ml of 20% wt. pure concentrated HNO₃ was added to the samples. These were used to determine major cations. A second sample set was collected but not acidified and was utilized for the analysis of major anions.

3.2. Laboratory Analyses

All chemical analyses were performed at the Laboratory of Volcanology and Geochemistry in Tokai University, Japan. The water samples were analysed for major cations (Ca²⁺, Mg²⁺, Na⁺, K⁺) by Flame Atomic Absorption Spectrometer (AAS) and major anions (F⁻, Cl⁻, NO₂⁻, NO₃⁻, Br⁻, PO₄³⁻, SO₄²⁻) by Ion Chromatography (ICS-900). Two replicates were run per sample. Overall, an ionic balance error of ± 5% was considered in further analysis and discussion.

The spatial distribution maps for major ions were compiled using the Inverse Distance Weighting (IDW) technique in ArcGIS10.2 which is based mainly on the distance between the sampling points (5 to 10 km). Other information such as geology and land use were used in interpreting element distributions within the basin.

4. Results and Discussions

4.1. Geochemical Data

Summary statistics for the streamwater data showing physico-chemical parameter measurements and major ion concentrations are presented in Table 1. Most streams of the Lom Basin were predominantly neutral to mildly acidic in nature with pH values between 5.0 and 7.3. Electrical conductivity varied from 9 to 112 µS cm⁻¹ and TDS ranged from 4 to 87 mg/L, with an average value of 27.98 mg/L. In agreement with [19] classification, all stream water samples in the study area were categorized as fresh (TDS < 1000 mg/L).

4.1.1. Major Ion Geochemistry

Calcium and Na⁺ were the dominant cations followed by K⁺ and Mg²⁺. The concentration of Ca²⁺ varied from 0.2 to 9.48 mg/L and accounted for 32% of the total cations. Concentrations of Na⁺ were higher than those of Ca²⁺ in 40% of the analysed water samples. In addition, Na⁺ and K⁺ contributed 52% of the total cations. Like Ca²⁺ and Na⁺, HCO₃⁻ was the dominant anion with a secondary contribution from NO₃⁻. The order of abundance was HCO₃⁻ >> NO₃⁻ > Cl⁻ >SO₄²⁻ > F⁻ >NO₂⁻ > Br⁻ > PO₄³⁻. Bicarbonate levels were between 2.73 and 62.66 mg/L with an average value of 19.41 mg/L and accounted for 95% of the total anions. Excess HCO₃⁻ can be ascribed to the weathering of alumino-silicate minerals [21–22] or the formation of carbonic acid when CO₂ resulting from the decay of organic matter combines with rainwater. The levels of NO₃⁻ in the samples were generally low (< 2 mg/L) and constituted 3% of the total anions. The only exception was sample GB-17 (NO₃⁻ = 20.01mg/L) collected from a stream flowing close to an established refugee camp in Gado Badzere. Common sources of dissolved NO₃⁻ in water include atmospheric precipitation, domestic sewage, agriculture fertilizers, human and animal...
The unexpected high NO\textsubscript{3}– observed suggested the contribution of nitrate by oxidation of human and animal nitrogeneous waste given that open air defecation and cattle farming in this area are practiced on a fairly large scale. Sulphate concentrations (0.01–0.57 mg/L) were lower than concentrations in natural water (2-80 mg/L) and reflect the low dissolution sulphide minerals in the near neutral waters. Besides, a negative correlation was observed between SO\textsubscript{4}2– and pH (table 2) suggesting that the mild acidity recorded in the streams could not have originated through sulphide oxidation but perhaps by pyrite oxidation. Also, it is possible that the acid generated during this process might have been consumed through reactions with silicate minerals thereby providing a long-term buffering capacity.

### Table 1. Descriptive statistics of physico-chemical parameters of stream water in the study area. Dissolved ion levels are compared to WHO proposed levels.

| Parameters | Units | Minimum | Maximum | Average | Standard deviation | WHO (2011) |
|------------|-------|---------|---------|---------|--------------------|------------|
| Temp | °C | 17.30 | 29.00 | 22.08 | 2.23 | 6.50-8.50 |
| pH | - | 5.00 | 7.30 | 6.26 | 0.47 | |
| EC | µS/cm | 9.00 | 112.00 | 36.42 | 30.31 | 500.00 |
| TDS | mg/L | 4.00 | 87.00 | 27.98 | 23.45 | 50.00 |
| Na\textsuperscript{+} | mg/L | 0.06 | 8.96 | 2.34 | 2.13 | |
| K\textsuperscript{+} | mg/L | 0.40 | 3.71 | 1.54 | 0.80 | 100.00 |
| Ca\textsuperscript{2+} | mg/L | 0.20 | 9.48 | 2.40 | 2.37 | 75.00 |
| Mg\textsuperscript{2+} | mg/L | 0.01 | 4.74 | 1.23 | 1.37 | 30.00 |
| HCO\textsubscript{3}– | mg/L | 2.73 | 62.66 | 19.41 | 17.29 | 200.00 |
| NO\textsubscript{3}– | mg/L | 0.01 | 20.01 | 0.75 | 3.23 | 50.00 |
| Cl– | mg/L | 0.07 | 1.28 | 0.23 | 0.21 | 250.00 |
| SO\textsubscript{4}2– | mg/L | 0.01 | 0.57 | 0.13 | 0.15 | 200.00 |
| F | mg/L | 0.01 | 0.21 | 0.07 | 0.05 | 1.00 |
| NO\textsubscript{2}– | mg/L | 0.00 | 0.13 | 0.04 | 0.03 | |
| Br\textsuperscript{–} | mg/L | 0.02 | 0.10 | 0.04 | 0.02 | |
| PO\textsubscript{4}3– | mg/L | 0.00 | 0.23 | 0.06 | 0.05 | |
| Na/Cl | - | 0.81 | 111.58 | 23.20 | 26.89 | |

### 4.1.2. Hydrogeochemical Facies of Streams

The chemical patterns of the streamwater were elucidated by plotting the major ions on a Piper [26] trilinear diagram (Figure 2). This produced two distinctive water types: 77% of samples plotted as CaHCO\textsubscript{3} and 23% as NaHCO\textsubscript{3}. These water species are typical of surface water draining igneous/metamorphic rocks in hot and humid equatorial climate, resulting in the discordant dissolution of primary silicate minerals such as Na-feldspars, plagioclases, pyroxene and hornblende [27–28]. Also, the water facies indicate short residence time thus low water-rock interaction [29], ion exchange and active recharge by groundwater associated with low EC [30].

![Figure 2. Piper trilinear diagram depicting the chemical species of streamwater in the study area. Streamwater is classified as Ca-HCO\textsubscript{3} and Na-HCO\textsubscript{3} water types.](image-url)
4.2. Geochemical Processes Controlling Surface Water Chemistry

Weathering of silicate and carbonate minerals is a primary source of alkalinity in natural water. Also, the stoichiometric relationships between dissolved species have been used to unravel the origin of solutes and the processes that influenced the observed water chemistry. To investigate the role of mineral weathering, [31] suggested the plot of total cations against alkalinity. Based on this method, a 1:1 relation between the sum of cations and alkalinity is an indication that mineral weathering is the primary process controlling the water chemistry.

In this study, all samples plot on or near the 1:1 dissolution line in Figure 3a indicating that silicate weathering is the main hydrogeochemical process affecting the surface water chemistry. These common rock-forming minerals are altered by the mildly acidic streamwater through hydrolysis to form metal cations in solution.

The role of other geochemical processes was investigated using NO$_3^-$ vs HCO$_3^-$ plot (Figure 3b). An insignificant negative correlation rules out the possibility of nitrate generating processes given that nitrification or oxidation of organic matter will produce an equivalent of NO$_3^-$ by consuming the same equivalent of alkalinity [31]. Moreover, [32] proposed that the plot of Ca$^{2+}$+Mg$^{2+}$ against HCO$_3^-$+SO$_4^{2-}$ will be close to the 1:1 line when carbonate dissolution is the dominant reaction in the system. However, in this study, all water samples plot below the theoretical equiline with a pronounced deviation at higher concentrations (Figure 3c). Higher HCO$_3^-$+SO$_4^{2-}$ content compared to Ca$^{2+}$+Mg$^{2+}$ indicated a significant contribution from non-carbonate sources. Also, the deficiency in the sum of alkaline earth metals relative to bicarbonate requires that the excess negative charge of the anions be balanced by Na$^+$+K$^+$ supplied through the weathering of Na-K silicates [33].

Figure 3. Mechanisms governing streamwater chemistry. (a) Relation between total cations and alkalinity showing silicate weathering (b) Variation in NO$_3^-$ concentrations as a function of alkalinity (c) Relation between Ca$^{2+}$+Mg$^{2+}$ and HCO$_3^-$+SO$_4^{2-}$ showing non-carbonate dissolution (d) Na vs. Cl cross plot. Sodium is derived from cation exchange.
The relationship between Na and Cl is frequently used to determine the source of salinity in natural waters. Besides, the stoichiometry of halite dissolution demands equal concentrations of Na⁺ and Cl⁻ in solution and a corresponding molar ratio of approximately one [33]. The molar ratio of Na⁺/Cl⁻ in the water samples compared to seawater (0.86) varied from 0.81 to 111.58 (average 23.2) with 98% of the samples showing Na enrichment. Higher Na⁺/Cl⁻ ratios (>1) reflect contributions from non-halite sources. From the 1:1 plot of Na⁺ against Cl⁻ (Figure 3d), an increase in Na⁺ without a corresponding increase in Cl⁻ was observed. This can be attributed to the possible exchange of Ca²⁺ for Na⁺ at clay surfaces or organic components of the soil resulting in the Na-HCO₃ water type. Organic matter and clay minerals have negatively charged ions which can adsorb and hold positively charged base cations by electrostatic force.

Furthermore, Pearson’s correlation matrix (table 2) was computed to determine the inter-element relationship. From the resultant matrix, pH revealed a negative correlation with most of the variables. The electrical conductivity showed a high correlation (r = 0.923) with TDS indicating its direct relationship to the amount of dissolved salts in water. Similarly, high positive r values were observed between HCO₃⁻ and the major cations. Chloride showed relatively high (0.84) and moderate (0.402) correlations with NO₃⁻ and SO₄²⁻, respectively. The underlying geochemical processes controlling the composition of stream water in the Lom Basin were investigated following principal component analysis (PCA) computation (table 3). Varimax rotation was adopted.

In PCA, eigenvalues are commonly used to identify the number of components (PCs) that can be retained for later study [34]. Only PCs with eigenvalues greater than unity were extracted for further analysis. Thus, three PCs were considered which accounted for 83.7% of the total variance of information of the dataset. Principal component 1 (PC1) comprised TDS-EC-HCO₃⁻-Mg²⁺-Ca²⁺-Na⁺-K⁺-pH and explained 59.7% of the total variance. The strong positive loading (>0.9) observed in this component suggested a common source, essentially the weathering of silicate minerals, and to some extent cation exchange. Carbonic acid facilitates the breakdown of silicate minerals. This reaction is accompanied by the release of base cations, silic acid and increased alkalinity [35] as observed in the study area. Potassium showed a moderate loading (0.652) suggesting K⁺ was removed from solution by clays in the formation of secondary minerals.

PC2 constituted Cl⁻ and NO₃⁻ which explained 14.2% of the total variance. A negative contribution from the other variables was also observed. The combination of these anions indicated their anthropogenic input through human-related activities such as sewage sludge and cattle rearing in the surrounding communities [29]. The third component composed of SO₄²⁻ and accounted for 9.8% of the total variance. This single variable correlated with the presence of sulphide bearing minerals and gold deposits. Gold occurs as quartz veins associated with vug-filling early pyritization in the Lom Basin [9].

4.3. Regional Spatial Distribution and Sources of Enriched Geochemistry

The regional geochemical maps for dissolved ions are presented in figures 4 to 12. Concentrations of Cl⁻ and NO₃⁻ (Figures 4 and 5) corresponded to high levels of H⁺ or low pH (Figure 6) in the northeastern portion of the study area which involves localities close to the volatile border between Cameroon and the Central African Republic. These localities host more than two hundred thousand refugees. Hence, the domestic waste water produced from these municipalities, stock-raising and open air defecation contributed to NO₃⁻ and Cl⁻ concentrations and account for the mild acidity recorded in water. Bicarbonate, Ca²⁺, Na⁺, K⁺, and Mg²⁺ showed similar distribution trends (Figures 7-11) basically indicating the underlying geology of the catchment area. These cations form the common silicate minerals alongside silicon and oxygen. Also, the incongruent dissolution of silicate minerals that react with dissolved CO₂ gas derived directly from the atmosphere, decay of organic matter in the soil or photosynthesis results in the release of major cations, bicarbonate and dissolved silica [36].

| pH  | 1   |     |     |     |     |     |     |     |     |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| EC  | 0.395* | 1   |     |     |     |     |     |     |     |
| TDS | 0.381** | 0.923** | 1   |     |     |     |     |     |     |
| Cl  | -0.007 | 0.234 | 0.264 | 1   |     |     |     |     |     |
| SO₄²⁻ | -0.004 | -0.109 | -0.137 | 0.402** | 1   |     |     |     |     |
| NO₃⁻ | -0.081 | 0.162 | 0.219 | 0.840** | 0.491** | 1   |     |     |     |
| HCO₃⁻ | 0.004 | 0.028 | 0.002 | 0.170 | 0.986** | 0.107 | 1   |     |     |
| Na⁺ | -0.022 | -0.078 | -0.107 | 0.401 | 0.999** | 0.356** | 0.990** | 1   |
| K⁺ | -0.092 | -0.040 | -0.106 | 0.177 | 0.934** | 0.150 | 0.965** | 0.948** | 1   |
| Ca²⁺ | 0.357** | 0.965** | 0.961** | 0.198 | 0.167 | 0.177 | 0.967** | 0.866** | 0.729** | 1   |
| Mg²⁺ | 0.313* | 0.978** | 0.970** | 0.219 | 0.157 | 0.139 | 0.978** | 0.908** | 0.705** | 0.938** | 1   |

*correlation is significant at the 0.01 level (2-tailed).
*correlation is significant at the 0.05 level (2-tailed).
Table 3. Varimax rotated component matrix analysis of streamwater parameters.

| Variable | Component 1 | Component 2 | Component 3 | Communalties |
|----------|-------------|-------------|-------------|--------------|
| TDS      | 0.997       | -0.002      | 0.022       | 0.552        |
| EC       | 0.995       | 0.033       | 0.001       | 0.992        |
| HCO₃⁻     | 0.994       | -0.035      | 0.019       | 0.994        |
| Mg²⁺      | 0.955       | 0.048       | -0.037      | 0.837        |
| Ca²⁺      | 0.954       | -0.080      | -0.015      | 0.634        |
| Na⁺       | 0.944       | 0.124       | -0.024      | 0.939        |
| K⁺        | 0.652       | -0.026      | 0.320       | 0.990        |
| pH        | 0.609       | -0.340      | 0.255       | 0.907        |
| Cl⁻       | 0.196       | 0.890       | 0.075       | 0.528        |
| NO₃⁻      | -0.142      | 0.780       | -0.077      | 0.917        |
| SO₄²⁻     | -0.011      | -0.010      | 0.969       |              |

Comparable findings have been reported in some natural waters of Cameroon [21, 37–38, 27]. These authors attributed the solute composition of natural waters to the hydrolysis of the rock-forming minerals and the incongruent weathering reactions. Contrary to the major cations, the distribution of SO₄²⁻ (Figure 12) correlated with the occurrence of sulphide minerals associated with Au mineralization in the area. Sulphidation of the wall rock has been proposed as a possible mechanism of hypogene gold precipitation within the Lom Group [9].

Figure 4. Streamwater regional geochemical baseline map of Cl⁻ concentration in southeastern Lom Basin. Dissolved ion concentrations are in mg/L.
Figure 5. Streamwater regional geochemical baseline map of NO$_3^-$ concentration in southeastern Lom Basin. Dissolved ion concentrations are in mg/L.
Figure 6. Streamwater regional geochemical baseline map of $H^+$ concentration in southeastern Lom Basin. Dissolved ion concentrations are in mg/L.
Figure 7. Streamwater regional geochemical baseline map of $\text{HCO}_3^-$ in southeastern Lom Basin. Dissolved ion concentrations are in mg/L.
Figure 8. Streamwater regional geochemical baseline map of Ca$^{2+}$ in southeastern Lom Basin. Dissolved ion concentrations are in mg/L.
Figure 9. Streamwater regional geochemical baseline map of Na$^+$ in southeastern Lom Basin. Dissolved ion concentrations are in mg/L.
Figure 10. Streamwater regional geochemical baseline map of $K^+$ in southeastern Lom Basin. Dissolved ion concentrations are in mg/L.
Figure 11. Streamwater regional geochemical baseline map of Mg$^{2+}$ in southeastern Lom Basin. Dissolved ion concentrations are in mg/L.
5. Conclusions

This study assessed the hydrochemistry of streamwater in the Lom catchment. The streamwater is mildly acidic to neutral in nature. Calcium and Na\(^+\) were the dominant cations and HCO\(_3^-\) was the most abundant anion. All the analysed parameters except pH were within the desirable limits (WHO) for drinking purposes. CaHCO\(_3\) and NaHCO\(_3\) were the main water types in the area signifying freshwater. In this research, the interrelationship among dissolved species have been used to determine the roles of different geochemical processes affecting the chemistry of streams draining the Lom Basin. Accordingly, the observed chemical composition of the streamwater was mostly influenced by the chemical weathering of the surrounding rocks. Cation exchange and anthropogenic activities were identified as minor geochemical controls.

The provenance of elements was distinguished based on geology and land use. Bicarbonate, Na\(^+\), Ca\(^{2+}\), Mg\(^{2+}\) and K\(^+\) showed similar distribution trends reflecting the geology. Sulphate distribution correlated with the occurrence of sulphides associated with vein gold deposits in the area. The distribution patterns of NO\(_3^-\) and Cl\(^-\) were attributed to pollution from settlements. These dissolved ions were considered to influence the acidity locally. The quality of surface water is easily influenced by anthropogenic activities,
and stream sediment collects effectively trace metals resulting from such activities. Therefore, geochemical mapping incorporating surface water and stream sediment is of considerable value in future investigations within the Lom Basin.

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