



# Seasonal Hydrological Inputs of Major Ions and Trace Metal Composition in Streams Draining the Mineralized Lom Basin, East Cameroon: Basis for Environmental Studies

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## Abstract

**Purpose** The aim of this study is to assess the seasonal variation in major ion distribution patterns and identify the origin and geochemical behavior of some trace metals of streamwaters bathing the mineralized Lom Basin.

**Methods** Eighty-one water samples were collected during the dry and wet seasons and analyzed for major ions using AAS and 12 trace metals (Fe, Mn, V, Cr, Co, Ni, Cu, Zn, As, Cd, Pb, Hg) by ICP-MS.

**Results** All physicochemical parameters besides pH and  $\text{Cl}^-$  varied narrowly between both seasons. No seasonal variability was observed for  $\text{Cl}^-$  given its conservative nature, while  $\text{NO}_3^-$  levels decreased in the wet period due to the dilution effect. Similarly,  $\text{SO}_4^{2-}$  concentrations were low for both seasons reflecting the dissolution of low sulphide minerals associated with gold deposits. In contrast, the concentration of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{HCO}_3^-$  slightly increased during the wet season as they are flushed from the soil layers by rain. Water samples had very low concentrations ( $< 1 \mu\text{g/l}$ ) of V, Cr, Co, Cu, Zn, Cd, Pb and significant concentrations of Fe and Mn.

**Conclusions** The seasonal regime of streamwater chemistry is controlled by groundwater supply of major cations and  $\text{HCO}_3^-$  from chemical weathering, leaching of ions from surface soil layers during precipitation and dilution of nitrate by surface runoff during the wet season. In this tropical basin, low acidity and trace metal loadings

revealed lateritic weathering of sulphides, entrapment of trace metals in Fe and Mn oxides and leaching into deep groundwater. Although the streams have not been impacted, these findings may guide policymakers for water chemistry evaluation in Cameroon.

**Keywords** Seasonal variation · Major ions · Trace metals · Lom Basin · Cameroon

## 1 Introduction

Hydrogeochemical processes help to unravel changes in surface water quality relating to water–rock interaction or anthropogenic impacts (Singh et al. 2005; Kumar et al. 2006; Franz et al. 2014; Nganje et al. 2015; Kamtchueng et al. 2016). The geochemical properties of surface water also depend on the chemistry of the recharging source as well as the various geochemical processes occurring within the drainage basin. The latter is often responsible for seasonal variations in surface water chemistry (Eneji et al. 2012); hence, the chemistry of streamwater flowing through a basin can evolve through interaction with weathering products and precipitation. In addition, dissolution and ion exchange reactions as well as anthropogenic actions including artisanal mining activities, which have the potential to damage the environment through water pollution, do play an important role in modifying the chemical composition of streamwater along flow paths (Hook 2005; Ako et al. 2014; Agyarko et al. 2014; Kpan et al. 2014; Simbarashe and Reginald 2014; Nganje et al. 2015; Rakotondrabe et al. 2017).

The Lom Basin constitutes part of the Precambrian ore deposits in Cameroon (Milesi et al. 2006). Undoubtedly, water is the principal transport route for dissolved solutes

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derived from both the chemical weathering of the mineralized basement and small-scale mining activities in the area. Streamwater and boreholes are the major sources of water supply for domestic and mining activities in this basin. Considering the importance of surface water in the area and the associated environmental problems with artisanal mining, Mimba et al. (2017) reported low concentrations of major ions and revealed that mineral weathering, ion exchange and anthropogenic inputs were the key factors influencing water chemistry. However, the seasonal hydrological inputs of these ions can be influenced by the growing population and increased mining activities within the catchment. Thus, seasonal estimation of dissolved ions is necessary to understand the contribution of ions and the long-term effects of changes in land use.

Trace metals are common environmental pollutants in mineralized drainage basins and their concentrations in streams can be of natural or anthropogenic origin. Small-scale mining, as well as the weathering of ore deposits, are well known to release elevated concentrations of trace metals into the soil and water systems (Van Straaten 2000; Nganje et al. 2011; Edet et al. 2014). Moreover, there are growing concerns about the impact of dissolved trace metals on the aquatic ecosystem and human health (Uwah et al. 2013; Dan et al. 2014; Bortey-Sam et al. 2015). No comprehensive survey has been conducted to determine metal levels in streamwater of the study area.

The present study, therefore, assesses the seasonal variation in major ion distribution patterns of streamwater and examines the origin and geochemical behavior of some trace metals in streamwater draining the lower Lom Basin.

### 1.1 Study Area

The study area is characterised by a mountainous relief that ranges from 600 to 1100 m above sea level. It is covered by shrubs and herbaceous savanna, and has a well-developed dendritic drainage. All examined streams flow within the basin and discharge into the Lom River which flows south-west, and eventually empties into the Atlantic Ocean. The area experiences the humid equatorial climate characterised by alternating dry (December to March, July to August) and wet (April to June, September to November) seasons with relatively high humidity and cloud cover (Braun et al. 1998; Neba 1999). Annual rainfall varies from 1500 to 2000 mm, while the mean temperature is 24.7 °C (Neba 1999). This typical tropical climate enhances prolonged chemical weathering of the parent rocks and the development of thick lateritic overburden.

In a geological context, the Lom Basin is a post-collisional basin dominated by younger volcanoclastic schists, metasedimentary rocks and ubiquitous S-type granitoids

which intrude the Pan-African basement (Soba et al. 1991; Toteu et al. 2001, 2006; Ngako et al. 2003). The tectonic evolution of this pull-apart basin and hydrothermal alteration around the plutons account for the widespread sulphide-bearing quartz vein gold deposits (Toteu et al. 2004). Accordingly, alluvial gold is worked from the streams draining this catchment (Omang et al. 2015). Small-scale gold mining constitutes the major industry in the area and dates back to the 1930s (Foumena and Bamenjo 2013). The study area encompasses the Garoua-Boulai and Betare-Oya towns with a total population of about 230,000. Over 80% of the inhabitants are subsistence farmers and depend on surface water and groundwater for domestic purposes.

## 2 Materials and Methods

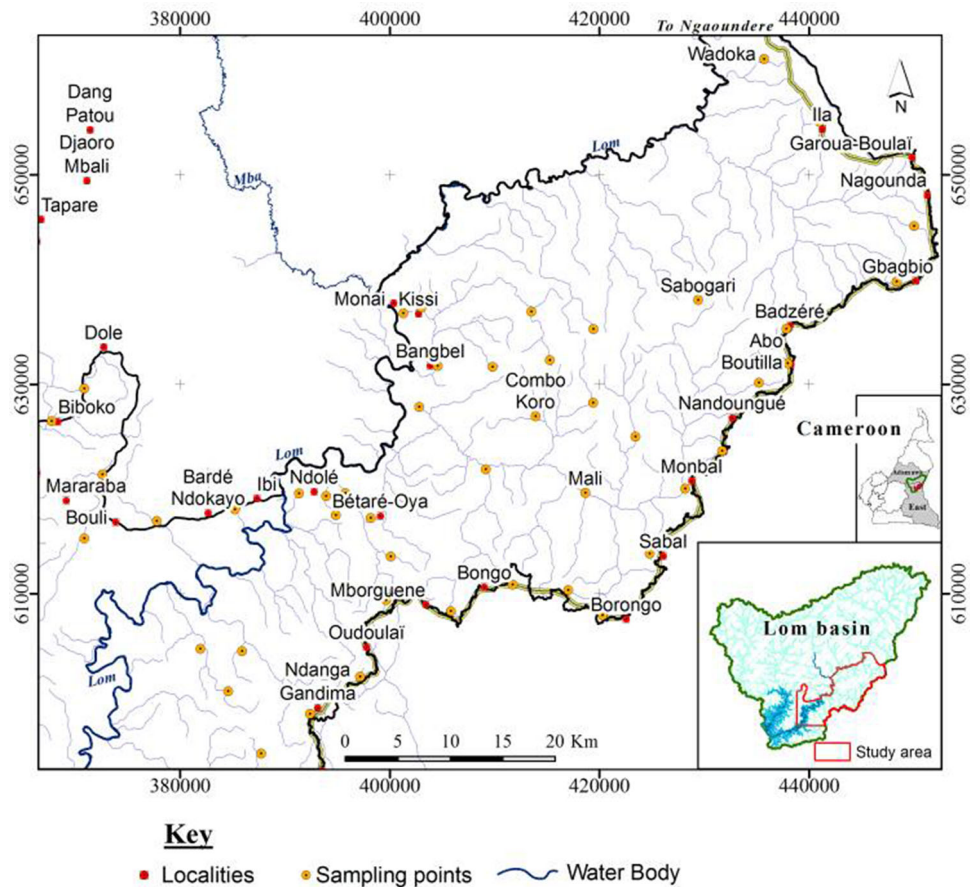
### 2.1 Streamwater Sampling and Field Measurements

Streamwater sampling was carried out during the dry (February to March) and wet (September to October) seasons in 2016, covering the lower Lom Basin (Fig. 1). During these surveys, 81 water samples were collected from lower order streams: 52 samples were collected during base-flow conditions and 29 samples during periods of high flow, for feasibility studies. Field sampling was done in accordance with the FOREGS (Forum of European Geological Surveys) Geochemical field mapping manual (Salminen et al. 1998). A sampling density of 1 sample every 5–10 km was used. The geographical parameters of each sampling site were obtained using a Garmin eTrex GPS. Field measurements were conducted for the physicochemical parameters including pH, electrical conductivity (EC), total dissolved solids (TDS), temperature using the HI 9811–5 Portable pH/EC/TDS/T meter, which was calibrated before and during the campaign. Alkalinity was conducted using a Hach field titration kit within 8 h of sample collection, whereby a volume of 0.16 N H<sub>2</sub>SO<sub>4</sub> was added dropwise to the sample, while continuously stirring with a pH meter to reach the end-point titration (pH 4.5). Water sampling within this tropical basin is discussed in detail elsewhere (Mimba et al. 2017). All samples were collected in previously-washed new 50-ml polyethylene bottles after rinsing severally with the sampled water prior to collection.

### 2.2 Major Ions and Trace Element Determination

Laboratory analyses were done at the Laboratory of Geochemistry and Volcanology at Tokai University, Japan. Streamwater samples were analysed for major cations (Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>) by flame atomic absorption spectrometer (AAS) (ContraAA700) and major anions (F<sup>-</sup>,

**Fig. 1** Location map of the Lom Basin indicating points of sample collection



$\text{Cl}^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{Br}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ) using ion chromatography (ICS-900). Laboratory standard solutions of these ions were prepared to calibrate the system. The cation-anion ionic balance error (Appelo and Postma 1996) was used to assess analytical precision. An ionic balance error within  $\pm 5\%$  and an overall precision better than 4% relative standard deviation were considered in further analysis and discussion. Trace element (Fe, Mn, V, Cr, Co, Ni, Cu, Zn, As, Cd, Pb, Hg) concentrations were determined by inductively coupled plasma mass spectrometry (ICP-MS) (ThermoScientific). Certified reference materials JA-3, JB-3, JG-3 (Japan Geological Survey) and blanks were simultaneously analysed to check for analytical precision and accuracy.

### 3 Results and Discussions

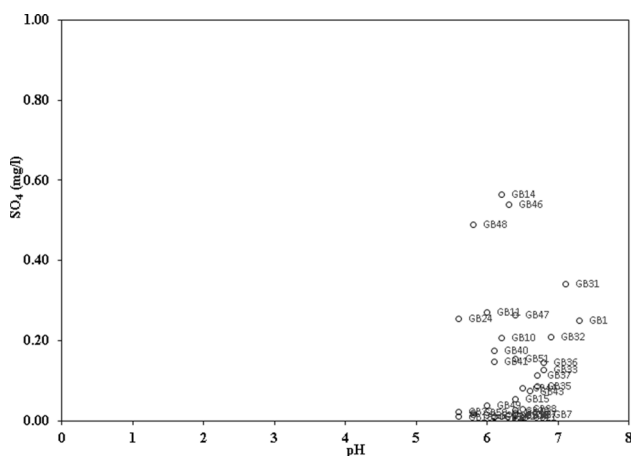
#### 3.1 Seasonal Variation of Major Ions

All analyzed parameters except pH and  $\text{Cl}^-$  showed a wide range of values between the sampling periods (Table 1). This seasonal variability suggests that diverse geological and geochemical conditions probably govern the observed

drainage signatures (Oman et al. 2014). Concentrations of  $\text{Cl}^-$ , which is of anthropogenic origin (Mimba et al. 2017), were invariable throughout the sampling seasons (Table 1) due to its conservative nature and limited potential sources (Grasby et al. 1997; Garizi et al. 2011). Like  $\text{Cl}^-$ ,  $\text{Na}^+$  showed only a slight increase during the rainy season. Contrarily,  $\text{NO}_3^-$  levels decreased in the wet period owing to dilution by surface runoff during periods of high flow. Sulphate loadings were low for both seasons. Sources of dissolved  $\text{SO}_4^{2-}$  in surface water include dissolution of  $\text{SO}_4$  minerals, oxidation of pyrite and organic sulphides in natural soil processes, and sulphur-based fertilisers (Hem 1985; Grasby et al. 1997; Kumar et al. 2006; Nganje et al. 2015). Since agricultural activities are practiced on a fairly small scale in this area, the use of sulphur-based fertilisers is not common. Furthermore, the cluster of points around the near neutral pH field and low  $\text{SO}_4^{2-}$  content (Fig. 2) is typically associated with low-sulphide gold quartz vein deposits (Ashley 2002). Thus, a plausible origin of dissolved  $\text{SO}_4^{2-}$  is the dissolution of sulphide minerals, excluding pyrite as a major source. Enhanced dissolution of these minerals and leaching of soils rich in iron oxides (Freyssinet et al. 1989) during the wet season accounts for the seasonal variations (Table 1) observed in the area.

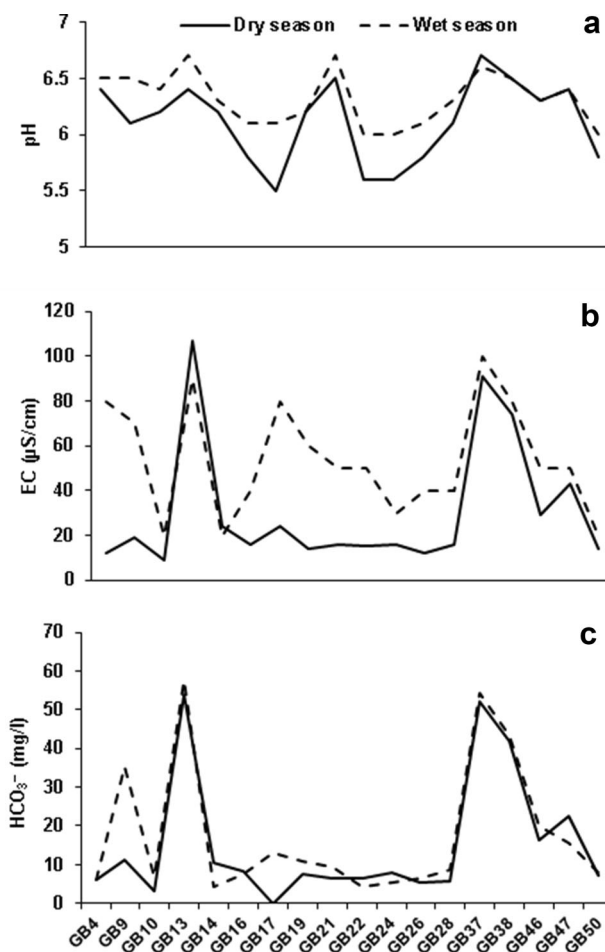
**Table 1** Seasonal variation of selected streamwater quality parameters

	Dry season			Wet season		
	Minimum	Maximum	Mean	Minimum	Maximum	Mean
pH	5.50	6.70	6.12	6.00	6.70	6.32
EC (μS/cm)	9.00	107.00	30.61	20.00	100.00	53.89
TDS (mg/l)	5.85	69.55	19.90	13.4	67.00	36.11
Na <sup>+</sup> (mg/l)	0.06	8.96	2.05	0.41	6.65	2.20
K <sup>+</sup> (mg/l)	0.63	2.53	1.36	0.47	3.65	1.91
Ca <sup>2+</sup> (mg/l)	0.20	8.52	1.95	0.40	7.69	2.00
Mg <sup>2+</sup> (mg/l)	0.01	4.59	0.94	0.06	3.57	0.92
Cl <sup>-</sup> (mg/l)	0.07	1.28	0.33	0.08	1.29	0.33
NO <sub>3</sub> <sup>-</sup> (mg/l)	0.01	20.01	2.02	0.02	11.25	1.44
SO <sub>4</sub> <sup>2-</sup> (mg/l)	0.01	0.57	0.15	0.13	1.39	0.67
HCO <sub>3</sub> <sup>-</sup> (mg/l)	0.01	54.12	15.18	4.15	57.55	17.63
Na/(Na + Ca)	0.10	0.88	0.49	0.38	0.80	0.56



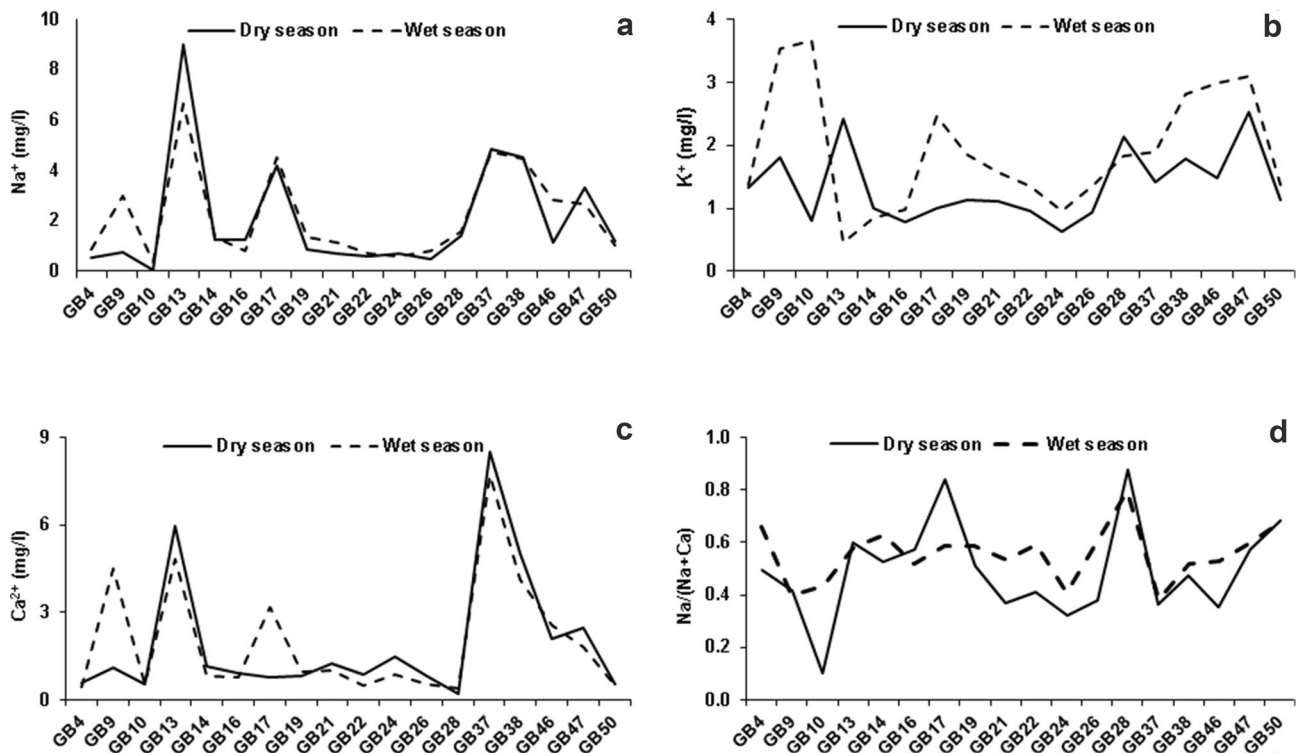
**Fig. 2** Low intensity of acid generation and SO<sub>4</sub><sup>2-</sup> concentration in the mineralized Lom Basin

Figures 3 and 4 show the evolution of streamwater chemistry in response to seasonal changes. Streamwater draining the Lom catchment remained near neutral (5.5–6.7) all year round although the pH increased by 0.2 units during the wet season (Table 1; Fig. 3a). Despite this uniform hydrogen ion activity, EC and HCO<sub>3</sub><sup>-</sup> were responsive to seasonal changes (Fig. 3b and c). These patterns revealed a shift from dilute (30.61 μS/cm) solution during the dry season to a solution with increased dissolved solids (53.89 μS/cm) during the months of heavy rainfall. An increase in the HCO<sub>3</sub><sup>-</sup> content during high-flow conditions of the wet season was also observed, neutralizing the mild acidity recorded during the dry season. In support of previous report by Mimba et al. (2017), the concentrations of Na<sup>+</sup>, K<sup>+</sup> and Ca<sup>2+</sup> slightly increased with increasing flow (Fig. 4a–c), exhibiting a similar seasonal pattern as HCO<sub>3</sub><sup>-</sup> alkalinity (Fig. 4c).



**Fig. 3 a–c** Seasonal trends showing an overall increase in pH, EC and alkalinity during the wet season. Dry and wet seasons correspond to periods of base flow and high flow, respectively. GB Garoua Boulai–Betare–Oya

It is well known that streamwater cation content usually increases during the dry season. During this period of low



**Fig. 4** Slight increase in Na<sup>+</sup>, K<sup>+</sup> and Ca<sup>2+</sup> concentrations in streamwater during the wet season **a–c**; **d** the mineral weathering indices for both seasons: Low Na/(Na + Ca) ratios indicate mineral weathering, while higher ratios signify other sources. GB, Garoua Boulai–Betare-Oya

stream discharge, high concentrations of major cations derived from silicate weathering are fed into the streams primarily by groundwater. With the advent of the wet period, stream discharge is expected to increase by surface or lateral flows during precipitation and dilute the streams (Meybeck 1987; Drever 1997; Khazheeva et al. 2007; Kelepertzis et al. 2012). Contrarily, a positive correlation was observed between solute concentration and stream discharge similar to observations for streams draining the Amazonian watershed in Brazil (Markewitz et al. 2001). The high levels of HCO<sub>3</sub><sup>-</sup> observed were attributed to the weathering of bedrock and the dissociation of carbonic acid resulting from increased root and microbial respiration during the wet season, with the latter generating the greater annual influx. In such tropical landscapes with highly weathered soils, the ratio of Na/(Na + Ca) has been used to determine the contribution of mineral weathering to streamwater cation content. Higher ratios indicate low rates of chemical weathering and vice versa. In the Lom Basin, the majority of samples had Na/(Na + Ca) ratios approaching one during the rainfall season and dropped during decreased flow (Fig. 4d). The mineral weathering index patterns (Fig. 4d) revealed that inputs from bedrock weathering dissolved in groundwater are predominant during base flow. In addition, slightly higher concentrations of major cations during the wet season are likely related to precipitation effects as they are flushed from soil surface

layers by heavy rainfall. Therefore, inputs of cations for the two sampling periods are derived from both the chemical weathering of primary minerals and their leaching from the cation-exchange complexes in surface soils.

### 3.2 Sources and Geochemical Behaviour of Trace Metals in Streamwater

The most significant metal loadings were those of Fe (20–5011 µg/l) and Mn (0.2–248 µg/l) reflecting metalliferous dissemination and weathering of pyrite within the basin. All water samples characterized by low concentrations (< 1 µg/l) of V, Cr, Co, Cu, Zn, Cd, Pb, and significant concentrations of As (up to 5.45 µg/l), Ni (up to 5.01 µg/l) and Hg (up to 4.98 µg/l) were within the WHO (2011) guidelines for drinking water (Table 2). The low levels and mobility of these elements are probably due to the very low aqueous solubility of the sulphide minerals in the ore deposits. Besides, these elements could likely be associated with suspended colloids or ferric oxides through adsorption phenomena (Smedley and Kinniburgh 2002). Trace metal loadings were lower than their mean concentrations in soils from the study area and the adjacent Batouri gold district (Table 2). In this strongly lateritic environment, the weathering of vein gold mineralization results in sulphide oxidation at the base of the profile. However, a significant portion of the trace metals released

**Table 2** Mean concentrations of trace metals ( $\mu\text{g/l}$ ) in streamwater compared to concentrations (ppm) in soils of the Betare-Oya and Batouri gold districts. The mean concentration of Fe in soils is expressed in wt% oxide

Element	Streamwater	Betare-Oya	Batouri	WHO (2011) in mg/l
Fe	6427.000	9.900	4.070	0.3
Mn	35.000	N/A	133.800	0.05
V	0.200	334.000	107.000	N/A
Cr	0.100	210.000	36.800	0.05
Co	0.300	N/A	2.900	N/A
Ni	0.400	N/A	3.600	0.07
Cu	0.010	N/A	9.000	2
Zn	0.001	N/A	9.000	3
As	0.800	60.000	2.100	0.01
Cd	0.001	N/A	0.300	0.003
Pb	0.020	125.000	11.000	0.01
Hg	0.200	N/A	N/A	0.006

Fe and Mn levels in some samples were above the WHO standards for drinking water. Data for soils from Betare-Oya gold district are adapted from Freyssinet et al. (1989) and for Batouri from Edith-Etakah et al. (2017)

N/A not available

in the soils are trapped as lattice components in secondary mineral phases such as ferruginous oxides (Freyssinet et al. 1989) and could be released by migration via adsorption, complexation and co-precipitation in a largely acidic environment. The overall low concentration of trace metals can also be attributed to leaching into deep groundwater. This is in agreement with the high levels of trace metals reported for wells within part of the study area (Rakoton-drabe et al. 2017).

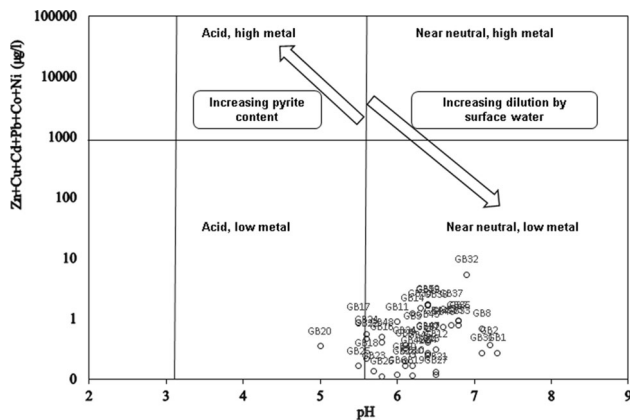
Principal component analysis (PCA) of metals in streamwater conducted produced four factors explaining about 70% of the total variance (Table 3). Factor 1 had strong positive loadings on Fe, V, Cr, pH, Ni and a strong negative loading on Zn. Factor 2 was made up of strong positive loadings on Mn, As and Co, while Factor 3 showed strong positive loadings of the elements Pb-Cu-Cd. These factors represent the oxidation and hydrolysis of sulphide minerals associated with gold deposits in the study area. However, in F1, Fe plays a major role in scavenging the other trace metals at low pH. The negative contribution of Zn suggests no co-precipitation effect of Fe on it. In contrast, Mn plays a major role in scavenging As in F2 which represents a different phase of mineralization (Omang et al. 2014). Also, Mn hydroxides have been reported to precipitate at high pH than Fe (Siegel 2002) which implies that Fe and Mn scavenge at different pH of streamwater within the Lom Basin. This is because the precipitation of Fe and Mn is pH-dependent, while that of trace metals depends on their co-precipitation with Fe and Mn. Higher concentrations of dissolved As compared to the chalcophile elements Cu, Zn, and Pb; and its disassociation from this group can be attributed to the weathering of arsenopyrite or the dissolution of metals from stream sediment in near neutral to

**Table 3** Factor analysis (with varimax rotation and Kaiser normalization) and total variance explained

Parameter	Factor			
	1	2	3	4
Fe	<b>0.739</b>	- 0.096	0.077	- 0.198
V	<b>0.735</b>	0.068	0.371	0.327
Zn	- <b>0.710</b>	- 0.233	0.258	0.021
pH	<b>0.636</b>	0.100	- 0.003	<b>0.516</b>
Cr	<b>0.635</b>	0.000	0.463	0.164
Ni	<b>0.515</b>	0.217	0.389	- 0.174
Mn	0.111	<b>0.908</b>	0.048	- 0.013
As	0.073	<b>0.805</b>	0.037	0.206
Co	0.005	<b>0.802</b>	0.053	- 0.208
Pb	0.297	0.160	<b>0.796</b>	0.156
Cd	- 0.191	- 0.130	<b>0.775</b>	0.003
Cu	0.425	0.341	<b>0.652</b>	0.223
Hg	- 0.057	- 0.055	0.161	<b>0.872</b>
Eigen value	4.254	2.098	1.570	1.130
% Variance	23.001	18.484	17.441	10.698
Cumulative % Variance	23.001	41.486	58.926	69.624

$N = 52$ . Values in bold represent loadings  $> 0.500$

slightly alkaline waters (Nganje et al. 2011; Kelepertzis et al. 2012). Under such pH conditions as observed in the study area, As becomes more mobile compared to other metals. Although arsenopyrite has been identified as a major sulphide mineralization event within this catchment, the relatively low dissolved concentrations of As can be related to its strong tendency to adsorb on hydrous Mn oxide mineral surfaces (Smedley and Kinniburgh 2002; Cheng et al. 2009). Factor 4 is composed of Hg and pH and



**Fig. 5** Ficklin's diagram of streamwater samples showing low base-metal content

could likely be as a result of its adsorption to very fine colloidal particles and dissolved organic matter, which could not be retained by the 0.45  $\mu\text{m}$  membrane filter. Besides, near neutral pH conditions and soil organic material tend to reduce Hg mobility (Van Straaten 2000). Gold amalgamation practiced illegally in the region has been reported as a possible source of Hg (Rakotondrabe et al. 2017).

The metal composition of the Lom catchment based on the traditional Ficklin diagram (Ficklin et al. 1992) is shown on Fig. 5. From this plot, it is obvious that low pH is necessary for significant high metal load to occur through sulphide oxidation. Most trace metals are amphoteric and tend to dissolve forming cations at low pH, or anions at high pH (Salomons 1995), than at the near neutral pH (5.5–6.7) condition of the study area whereby the transport of most suspended and dissolved trace metals is expected to be attenuated (Cravotta 2000). Thus, the neutral pH of the streamwater accounts for the low dissolution of trace metals. Besides, greater dilution and reduced solid to water ratio occurs in wetter climates such as in the tropics. These processes result in the generation of surface water from acid generating deposits such as sulphides with low acidity and trace element content (Plumlee and Logsdon 1999). Hence, despite the past and active small scale mining operations within this area, acid generation remains low and this accounts for the low concentrations of dissolved trace metals. On the other hand, there is also a possibility that the acid generated from sulphide weathering may have been consumed through reactions with silicate minerals (long-term buffering capacity) occurring in the parent rocks (Salomons 1995). In summary, the rate of acid generation is usually determined by chemical factors such as pH, temperature, gaseous and aqueous oxygen concentrations, chemical activity of ferric iron and the surface area of exposed metal sulphides as well as biologic parameters.

## 4 Conclusions

For the first time, the seasonal variation of major ions and trace metal concentration of streamwater in the lower Lom Basin have been investigated. From this study, the following observations were made:

- All measured physicochemical parameters showed no pronounced variation between the dry and wet seasons.
- Overall, the seasonal pattern of streamwater chemistry is controlled by three key processes: (a) contribution of major cations and  $\text{HCO}_3^-$  from chemical weathering supplied by ground water flow, (b) leaching of salts from surface soil layers during rain events and (c) dilution by surface runoff during the wet season.
- Trace element geochemistry revealed very low concentrations of V, Cr, Co, Cu, Zn, Cd, Pb and are attributed to deep chemical weathering and leaching into the groundwater.
- Iron and Mn concentrations in most samples exceeded the WHO (2011) guideline values for drinking water and are associated with the occurrence of pyrite. The dissolution of sulphides into the drainage system is the principal source of base metals in streamwater.
- Arsenic is believed to be leached from a different mineralization source and co-precipitated with Mn owing to its disassociation from the base metals Cu, Zn and Pb.
- Drainage signatures of the basin are marked by low acidity,  $\text{SO}_4^{2-}$  levels and base metal loadings reflecting low sulphide solubility and the likely buffering capacity of silicate minerals.

Although this study showed a relatively low seasonal variation in dissolved solutes, identifying the sources and processes governing their contribution is necessary for understanding the effects of future land use changes in the study area. Besides, despite many years of past and present small-scale mining activities, the area is currently under no risk of contamination by trace metals. Nonetheless, these findings may be considered by policymakers as a reference for setting safe limits and continuous monitoring of mining activities in the Lom Basin and other mineralized areas in Cameroon.

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