

## Hydrogeochemistry and groundwater flow mechanisms in shallow aquifer in Yaoundé, Cameroon

Alain Fouépé Takounjou, Gloria Takem Eyong, Dorice Kuitcha, Robert Kringel, Wilson Fantong Yetoh, Josephine Ndjama and Alex Tejiobou

### ABSTRACT

Hydrogeochemical processes and flow mechanisms of groundwater in the urban area of Yaoundé were investigated using major chemical constituents, stable isotopes ( $^{18}\text{O}$  and  $^2\text{H}$ ), and multivariate statistical analysis. Thirty five groundwater samples were collected and analysed for various parameters. Hydrogeochemical evolution visualized with the Gibbs diagram showed that the groundwater is mainly controlled by water–rock interactions. Factor analysis on the other hand identified three major groups of geochemical constituents and showed that weathering and anthropogenic inputs are the dominant factors controlling groundwater chemistry in the study area. Isotopic analyses revealed that oxygen-18 of groundwater ( $^{18}\text{O} = -2.96\text{‰ VSMOW}$ ) is close to that of rainfall ( $^{18}\text{O} = -2.47$ ), indicating that the groundwater is recharged by rainwater without evaporation. The geogenic composition of urban groundwater in Yaoundé is modified by secondary processes and anthropogenic input.

**Key words** | factor analysis, hydrogeology, silicate weathering, stable isotope, Yaoundé

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### INTRODUCTION

Groundwater is generally recharged by rainwater. The chemical composition of rainwater recharging the aquifers will change depending on factors such as geology, chemical reactions, aquifer structure, residence time and anthropogenic impacts (Hendry & Schwartz 1990). Mathematical and graphical approaches are generally used for the identification of geochemical constituents of a given groundwater sample. The mathematical approach is often used for the calculation of saturation indices of groundwater (Gupta *et al.* 2008). Additionally, a detailed picture of the groundwater system can be provided by the interpretation of the hydrochemical characteristics and the environmental isotope records of precipitation, surface water and groundwater (Prasanna *et al.* 2010). Stable  $^{18}\text{O}$  and  $^2\text{H}$  values of water are particularly useful for tracing the history

and origin of groundwater (Aggarwal *et al.* 1997). Generally, groundwater retains its stable isotopic signature unless diluted or mixed with waters of different isotopic composition, or if warmed above  $60\text{ °C}$  (Randall *et al.* 2005). Recently, hydrochemistry and the isotopes method was used by Wang *et al.* (2015) to reveal the mechanisms of groundwater evolution and also provide a method to identify nested flow systems in the Ordos watershed in China. Similarly, Beaudry *et al.* (2018) used the same method in southern Quebec to identify the mechanisms controlling groundwater composition and to support the understanding of the aquifer hydrodynamics. They stated that geochemical interpretation provided indications on regional recharge and discharge zones as well as groundwater flow, which could not have been determined otherwise.

There have been some attempts to study the groundwater mineralization and recharge in the Yaoundé urban area. For example, changes in groundwater chemistry along the flow path from the recharge areas towards the discharge areas in Yaoundé have been reported by [Kuitcha \*et al.\* \(2013\)](#), [Fouébé Takounjou \*et al.\* \(2013\)](#) and [Fantong \*et al.\* \(2013\)](#).

However, these studies are localized and generally use the aquifer characteristics (the physical and bacteriological composition of both surface water and groundwater). Nevertheless, in their study on the anthropogenic water types in urban groundwater nutrients in Yaoundé, [Kringel \*et al.\* \(2016\)](#) tried to link the field of study with a relatively natural environmental area, the Nsimi Experimental Watershed (NEW), situated less than 100 km south-south-east of Yaoundé. The natural elemental concentration of groundwater for this undisturbed forested site is reported in [Braun \*et al.\* \(2005\)](#). These data were used to constrain the anthropogenic influence on the data collected in Yaoundé. In the present study, carried out within the framework of the German–Cameroonian bilateral technical cooperation, EPSS 2013, major ion geochemistry and the stable hydrological isotopes were integrated to identify the underlying hydrogeochemical processes and the flow mechanism of groundwater in the urban area of Yaoundé.

## MATERIALS AND METHODS

### Study area

Yaoundé city is located at about 250 km of the Atlantic Ocean, within latitudes 3°83′–3°92′N, and longitudes 11°48′–11°52′E ([Figure 1](#)). The climate is equatorial with four seasons: a long dry season (from mid-November to mid-March), a short rainy season (from mid-March to mid-June) a short dry season (from mid-June to mid-September) and a long rainy season (from mid-September to mid-November). The annual average rainfall is about 1,600 mm and the mean annual temperature is 23 °C ([Sighomnou 2004](#)).

The city of Yaoundé is drained by three perennial rivers (the Mfoundi, Mefou and Mfoulou). Its vegetation is mainly composed of secondary forest, which is under continuous stress from farming and habitation. The topography is

undulating, with seven prominent hills which rise to a maximum height of about 1,060 m above sea level, with an average altitude of 800 m above sea level.

Southern Cameroon, which contains the study area, is underlain by two rock units, namely (i) the neo-proterozoic group of Yaoundé series, which is thrust onto the Congo Craton, and (ii) the Bafia group, which is classically assumed to be a palaeo-proterozoic tectonic slice of the basement that over-thrust the Yaoundé group to the north ([Vicat \*et al.\* 2002](#); [Tchakounté \*et al.\* 2007](#)). Metamorphic rocks such as gneiss, migmatites, and schists make up the basement of the south Cameroon plateau ([Nzenti \*et al.\* 1998](#)). Outcrops of these rocks appear along fault lines south of Yaoundé, where schists and quartzites are exposed. The migmatites of Yaoundé consist essentially of anatectic meta-pelitic kyanite-garnet gneisses characterized by granulite-facies mineral assemblages.

The region of Yaoundé is located on strongly weathered and intensely fractured metamorphic rocks. The weathered zone (15–20 m thick) is made up of clay and is acidic. The flow of groundwater may be following the major geological features (faults, fractures). The shallow aquifer is found in the thick layer of the weathered zone between 3 and 20 m depth. Depending on the porosity and the hydraulic conductivity observed by [Fouébé Takounjou \*et al.\* \(2012\)](#) ( $10^{-4}$  to  $10^{-6}$  m/s); this water table is important and has a regional extension. Owing to the undulating character of the topography, this water table often gives rise to springs ([Figure 2](#)). The shallow aquifer supplies wells and springs used by a substantial portion of the population. The traditional wells are located mainly in lowlands. With few exceptions, spring flows are low, varying from 0.7 to 5 m<sup>3</sup>/h ([Fouébé Takounjou 2012](#)) and do not permit large-scale utilization. The proximity of these waters to the surface makes them vulnerable to pollution.

The deep aquifer shelters the most important water resource; it is the least vulnerable but one whose mobilization is the most expensive. This aquifer is made up of complex fractures set up during the successive tectonic phases. These fractures create a network in which percolated water accumulates and flows out. The relatively high transmissivity ( $6.54 \cdot 10^{-7} \text{ m}^2/\text{s} \leq T \leq 1.6 \cdot 10^{-4} \text{ m}^2/\text{s}$ ) observed in these fractured aquifers makes them attractive targets of drilling campaigns ([Fouébé Takounjou \*et al.\* 2012](#)).

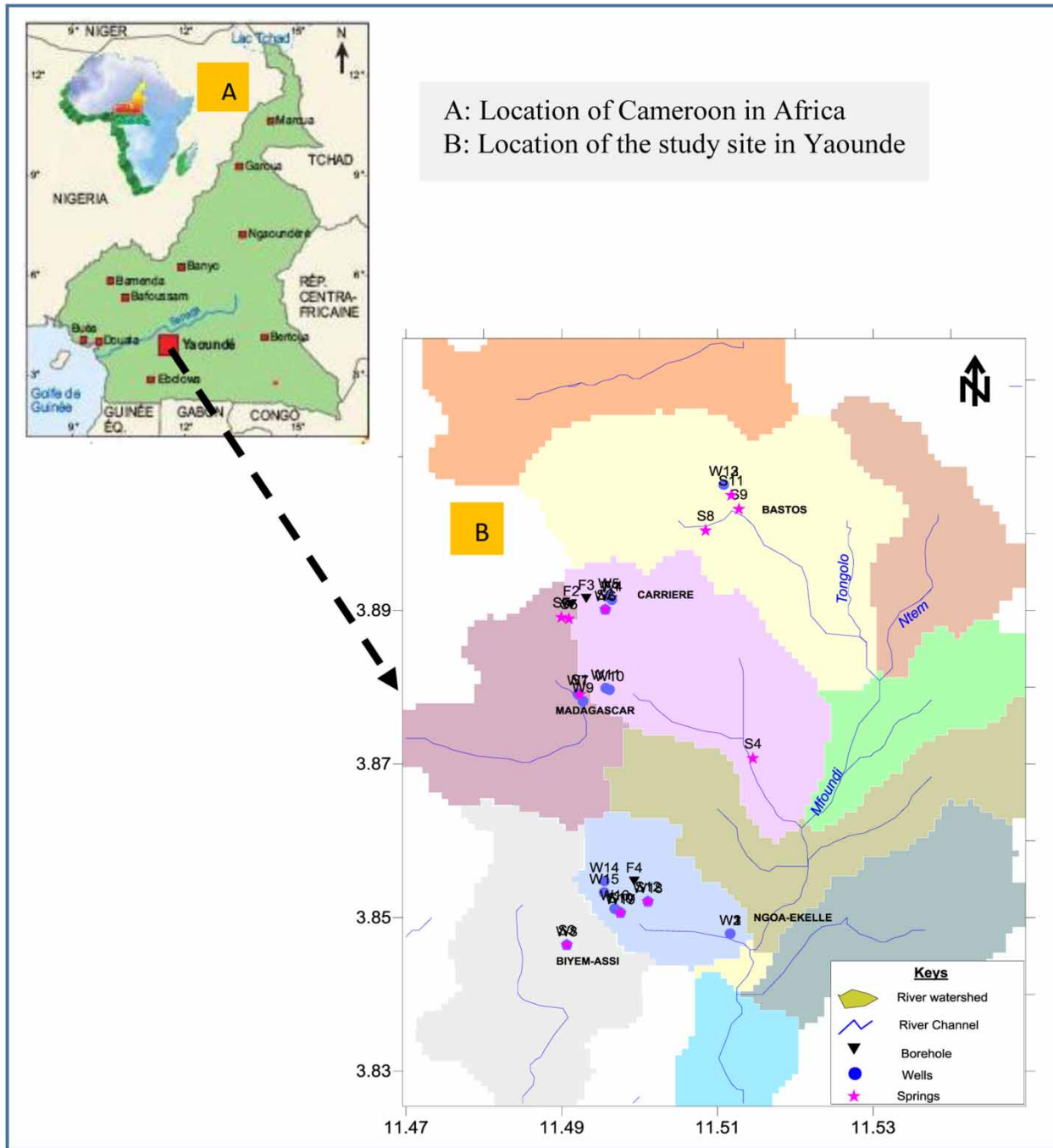
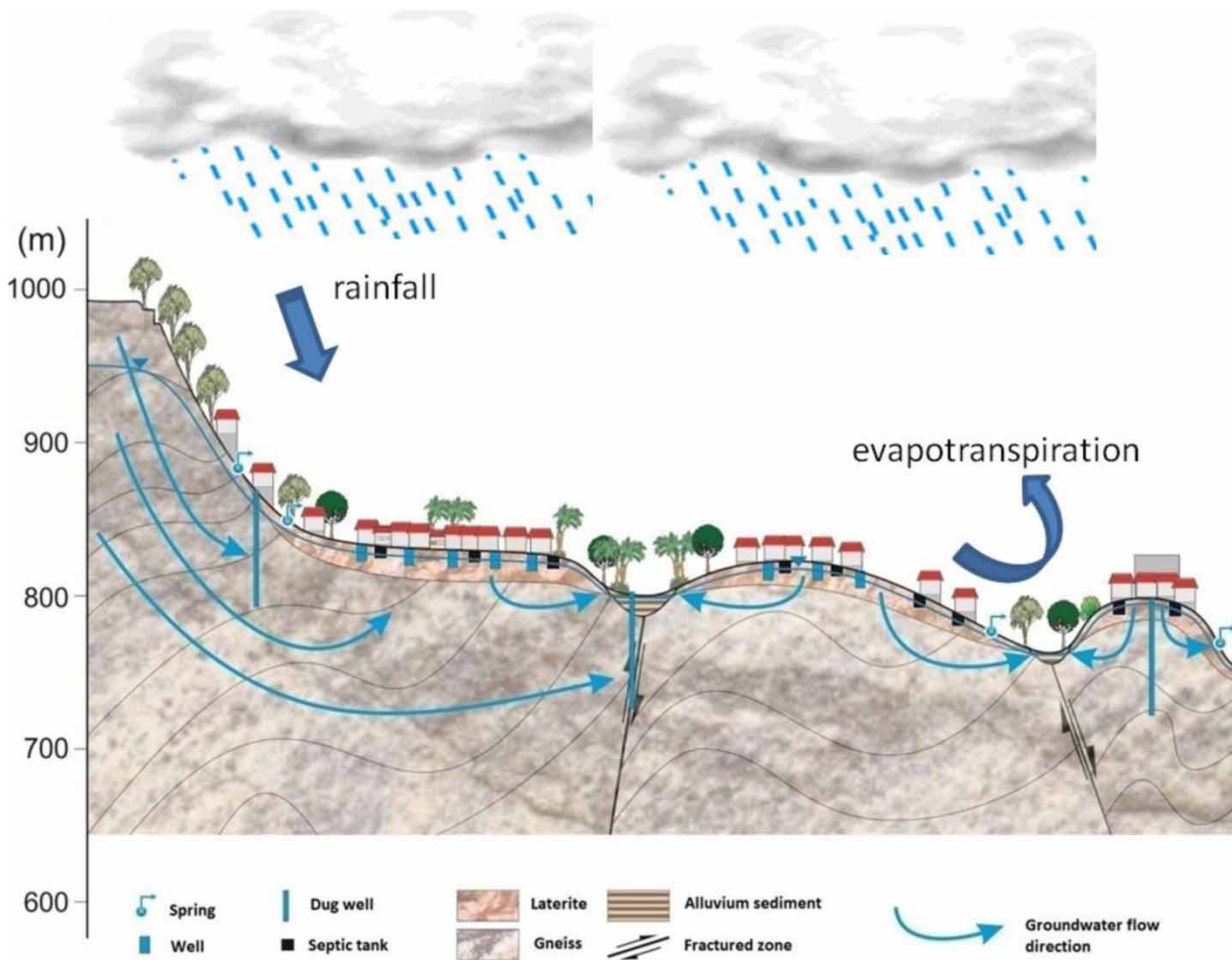


Figure 1 | Location map of the study area with sampled points.

### Sampling and analytical methods

The purpose of groundwater sampling was to collect samples that were representative of the subsurface

conditions. Desk study led to the selection of five spatial clusters for water sampling, namely: Ekoudou, Messa, Madagascar, Ngoa-Ekele and Biyem-Assi. A sampling campaign was carried out in April 2012, when 35 groundwater



**Figure 2** | Sketch of the water cycle to include the hydrogeological arrangement of terrain, aquifers and drainage network of Yaoundé in relation to urban settlement and decentralized installations of water supply and discharge. Flow lines are only approximate, not to scale.

samples (from 12 springs, 19 wells, four boreholes) were collected (Figure 1) and analysed. Water samples were collected in sterilized tubes and hermetically sealed to avoid accidental contamination. A photograph (or sketch) was used to describe the environment of each water point. *In-situ* parameters were recorded with a portable multi-parameter type Multi 340i: (pH, conductivity, salinity and temperature). Water samples were taken only after the above parameters were stabilized. All samples were placed in Pyrex glass bottles (for chemical analyses), labelled and stored in coolers.

Major elements and stable isotopes were analysed in the laboratory of the Federal Institute for Geosciences and Natural Resources (BGR), in Hanover, Germany. The

stable  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  were measured with a cavity ring down spectrometer type L2120-i (Picarro) laser spectrometer. Each sample was injected using a 10  $\mu\text{L}$  syringe. After each injection the syringe was washed three times with deionized water. The signal levels for all samples were in the required range for the instrument and varied between 19,000 and 21,000 ppmv. The  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values of the samples were normalized to the VSMOW scale (Vienna standard mean ocean water), following a three-point normalization. All laboratory standards were calibrated against international reference materials using the VSMOW-SLAP scale. The analytical precision reported by the manufacturer for this version of the instrument is 1.0‰ for  $\delta^2\text{H}$  and 0.10‰ for  $\delta^{18}\text{O}$ .

The major ions analysed include chloride ( $\text{Cl}^-$ ), sulfate ( $\text{SO}_4^{2-}$ ), nitrate ( $\text{NO}_3^-$ ), calcium ( $\text{Ca}^{2+}$ ), magnesium ( $\text{Mg}^{2+}$ ), sodium ( $\text{Na}^+$ ), potassium ( $\text{K}^+$ ), silica ( $\text{H}_4\text{SiO}_4$ ) and aluminium ( $\text{Al}^{3+}$ ). Fluoride, sulphate and nitrite were analysed using an ion chromatograph ICS 3,000 (Dionex). Alkalinity was determined by automated titration with 0.02 N HCl. Ammonium was determined using a photometer Unicam UV300 (Thermo Electron Corporation). Chloride and bromide were analysed via inductively coupled plasma optical emission spectrometry using a CiroS by Spectro.

In this paper, mathematical and graphical diagrams were used to assess the functional sources of natural dissolved chemical constituents, such as precipitation, rock, and evaporation dominance. Saturation indices (SIs) were calculated using the computer geochemical program WATEQF written by [Plummer \*et al.\* \(1976\)](#). Multivariate statistical analysis was used to group groundwater samples and

make correlations between chemical parameters, in order to investigate their sources and the processes with which they are associated ([Prasanna \*et al.\* 2010](#); [Adomako \*et al.\* 2011](#)). In this study, correlation and factor analyses are applied using statistical package of social studies (SPSS). This study also used previous work on aquifer properties, groundwater flow and mass transport modelling, carried out in part of Yaoundé city, to strengthen the understanding of the groundwater flow mechanism.

## RESULT AND DISCUSSION

### General hydrochemistry

The statistical results for groundwater chemistry are presented in [Table 1](#). The pH of the water samples ranged from 4.6 to 8.9

**Table 1** | Statistical summary data of physicochemical parameters of groundwater in the Yaoundé area

Parameters	Min	p10	p25	p50	p75	p90	Max	no	s.d.
Li (mg/l)	0.001	0.001	0.001	0.001	0.001	0.003	0.009	37	0.001
Ni (mg/l)	0.001	0.001	0.001	0.004	0.005	0.007	0.019	37	0.003
BO <sub>2</sub> (mg/l)	0.003	0.010	0.010	0.010	0.030	0.049	0.22	37	0.037
PO <sub>4</sub> (mg/l)	0.01	0.01	0.01	0.01	0.01	0.03	1.6	37	0.27
Fe (mg/l)	0.003	0.004	0.008	0.020	0.118	1.38	13.8	37	2.703
Al (mg/l)	0.004	0.004	0.011	0.024	0.047	0.096	0.256	37	0.050
Br mg/l)	0.004	0.010	0.018	0.061	0.103	0.138	0.21	37	0.05
Sr (mg/l)	0.01	0.018	0.024	0.063	0.10	0.15	0.29	37	0.06
F (mg/l)	0.014	0.031	0.049	0.079	0.108	0.196	0.974	37	0.157
Mn (mg/l)	0.01	0.07	0.10	0.25	0.9	1.5	5.1	37	1.03
TOC (mg/l)	0.03	0.03	0.03	0.50	1.10	2.5	13.20	37	2.4
NH <sub>4</sub> (mg/l)	0.000	0.004	0.64	1.89	10.7	40.7	80.4	37	18.7
SO <sub>4</sub> (mg/l)	0.10	0.44	0.9	1.9	6.8	15.3	21.0	37	6.1
Mg (mg/l)	0.2	0.9	1.8	5.0	9.0	10.7	15.2	37	4.1
Ca (mg/l)	1.0	2.23	3.45	5.33	10.8	13.73	55.8	37	11.0
K (mg/l)	1.1	1.4	3.25	5.5	12.0	22.1	64.6	37	11.57
SiO <sub>2</sub> (mg/l)	2.5	4.2	5.5	8.4	10.5	13.0	48.5	37	9.6
Na (mg/l)	1.9	7.0	9.8	23.4	51.8	64	141	37	31.1
HCO <sub>3</sub> (mg/l)	1.8	5.5	12.5	27	53	163	548	37	109
Cl (mg/l)	0.8	3.7	12.1	27.0	58.5	74.4	220.0	37	42.6
NO <sub>3</sub> (mg/l)	0.003	1.5	22.1	51.2	99.9	125.1	161.0	37	45.8
EC (µs/cm)	33	75	180	325	556	841	1,410	37	336.0

p: percentile; no: number of samples; s.d.: standard deviation.

with a mean value of 6.1, giving a total of 97% of groundwater samples that were acidic ( $\text{pH} < 7$ ). This acidity can be explained by the crystalline nature of the bedrock, which is composed of rock such as granite, gneiss and schist. Electrical conductivity (EC) and total dissolved solids (TDS) ranged from 23 to 1,410  $\mu\text{S}/\text{cm}$  and from 27.4 to 1,022.4  $\text{mg}/\text{l}$ , respectively. The high standard deviations of 336 and 181 for EC and TDS, respectively, indicated that the ions had different sources. The results for the cations showed that  $\text{Na}^+$  ranged from 1.9 to 141  $\text{mg}/\text{l}$ ,  $\text{K}^+$  ranged from 1.1 to 64.6  $\text{mg}/\text{l}$ ,  $\text{Ca}^{2+}$  ranged from 0.9 to 55.8  $\text{mg}/\text{l}$  and  $\text{Mg}^{2+}$  from 0.2 to 15.2  $\text{mg}/\text{l}$ .  $\text{SiO}_2^{2+}$  concentrations ranged from 2.5 to 48.5  $\text{mg}/\text{l}$  with a median 50th percentile (p50) value of 8.4  $\text{mg}/\text{l}$ . The results for the anions indicated that the concentrations in  $\text{mg}/\text{l}$  of  $\text{HCO}_3^-$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  ions were 1.8–548; 0.1–161; 0.8–129 and 0.1–21.2, respectively.

Based on the mean values of the chemical parameters, cations were in the order of abundance:  $\text{Na} > \text{Ca} > \text{K} > \text{Si} > \text{Mg}$ ; and anions:  $\text{NO}_3 > \text{Cl} > \text{HCO}_3 > \text{SO}_4$ . The high concentration of  $\text{NO}_3$  and  $\text{Cl}$  in the groundwater probably indicated an anthropogenic impact, such as sewage effluent, residue of household solid wastes and application of chemical fertilizers in urban agriculture (Fantong *et al.* 2013; Fouébé Takounjou *et al.* 2013; Kuitcha *et al.* 2013). Chloride could not have resulted from evaporite sources because they are unlikely in the area. The Yaoundé area is far from the coast (about 250 km), eliminating the option of sea spray and sea water intrusion as possible sources of chloride in the area.

Comparing the results of this urban site to the forested rural environment of NEW, the cation concentration was found to be almost in the same order of abundance  $\text{Na} > \text{Ca} > \text{Mg} > \text{K}$ , except that silica was the predominant chemical species and represented 70% of the dissolved load in NEW (Braun *et al.* 2005). The authors showed that silica is stored as residual quartz and secondary kaolinite crystals and is essentially transferred in a soluble rather than in a solid form, whereas the base cations are strongly depleted. The nitrate and sulfate content were below the detection limit in NEW (Braun *et al.* 2005), whereas nitrate was the most abundant anion in the present study. Put together, these facts strengthen the choice of the NEW chemical values as the geogenic background for this study.

The Stiff diagram of samples from each cluster displays the relative proportions of the major ions. The size indicates

the total concentrations and clearly shows the differences and similarities between the clusters (Figure 3). Except for the sample from Nkomkana, which shows visual abnormalities, the other samples are quite similar on the anion side but differ on the cation side due to higher concentrations of Ca and K.

The relative size of  $\text{HCO}_3$  with respect to the other species (Table 1) could be an indication of chemical weathering processes taking place in this aquifer. Percolating groundwater inducing silicate mineral weathering generally enhances Na and  $\text{HCO}_3$  concentration in groundwater (Rogers 1989). However, in crystalline terrains, weathering usually takes place to a very limited extent because of the limited quantity of weatherable material. Natural processes such as the incongruent dissolution of silicates that react with  $\text{CO}_2$  gas from root respiration and aqueous  $\text{CO}_2$  could be a mechanism that releases Na and K into the groundwater.

In order to identify the different sources of ions that constitute the water composition in Yaoundé, correlations between major ions were made using Spearman's correlation analysis. The results are shown in Table 2. Strong positive correlation ( $r = 0.76$ ) was found between Na and Cl, which is generally related to the process of sea water intrusion (Prasanna *et al.* 2010). This was, however, not the case here since the area is very far from the coast. In the absence of a geogenic source of chloride in the area, the presence of chloride in water samples could be from anthropogenic sources. Positive correlations also exist between dissolved silica and both  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ( $r = 0.59$  and  $r = 0.46$ , respectively). The correlation of  $\text{HCO}_3$  content with major cations suggests leaching of the host granitic rocks by  $\text{CO}_2$ -charged recharging waters. TDS was positively correlated to  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ , suggesting that TDS was derived mainly from these ions.

### Cluster and principal component analysis

The result of the hierarchical cluster analysis (HCA) is presented as a dendrogram in Figure 4. Based on the clusters, the groundwater samples were classified into three major groups. The Nkomkana well sample (case 23) belongs to group 3, while the Biyem-Assi and Madagascar well samples (case 20 and 21) are within group 2; the rest of the samples constitute group 1.

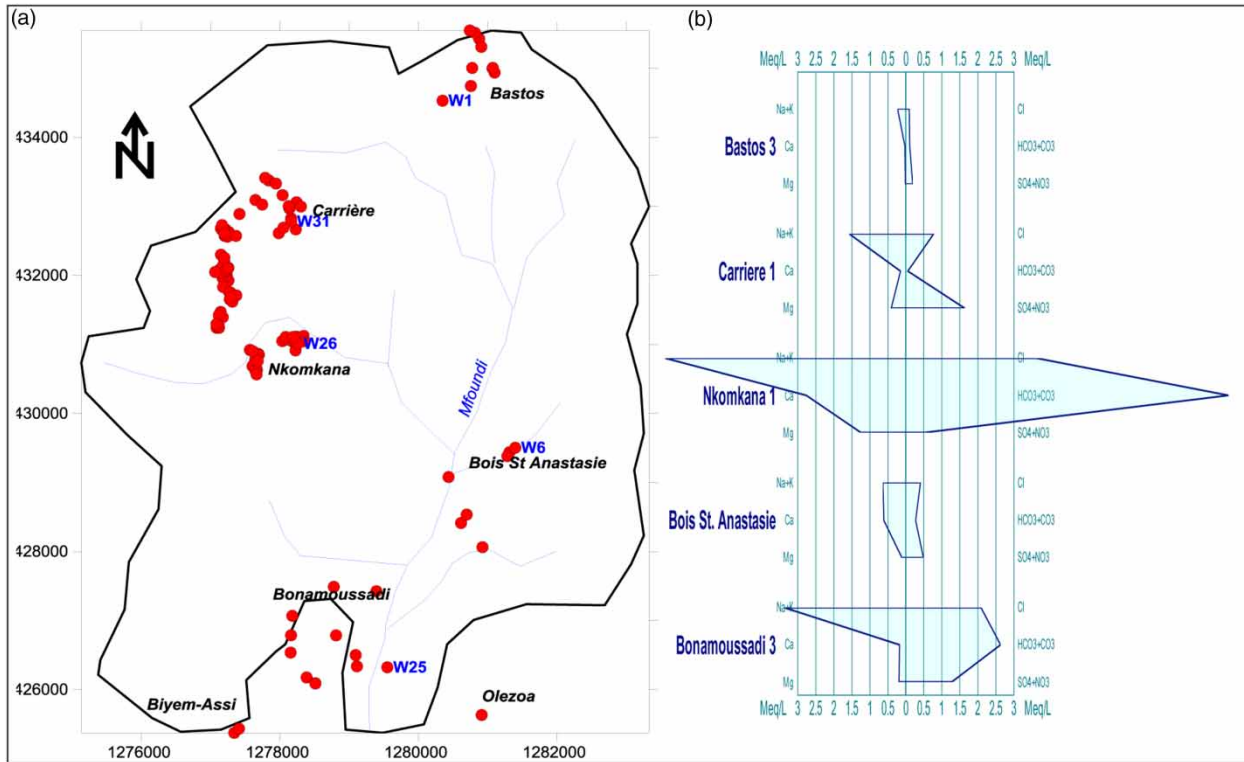


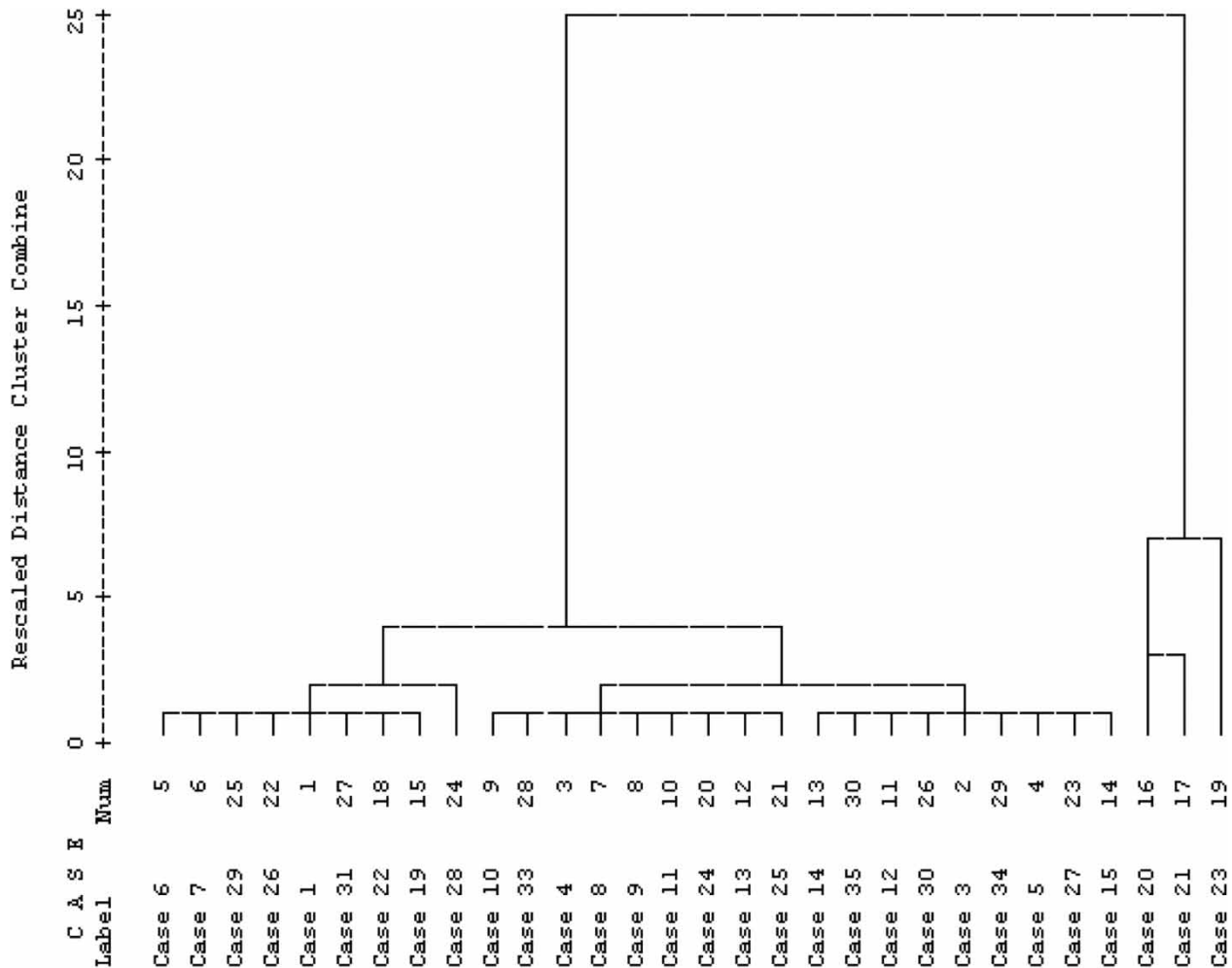
Figure 3 | (a) Location of sampled points and (b) Stiff diagrams of some samples indicating changes in chemical constituents of groundwater within the study area.

Table 2 | Correlation matrix among the 12 physico-chemical variables of the groundwaters

	TDS	T	pH	Ca	Mg	Na	K	HCO <sub>3</sub>	Cl	SO <sub>4</sub>	NO <sub>3</sub>	SiO <sub>2</sub>
TDS	1											
T	-0.1	1										
pH	0.57	0.01	1									
Ca	<b>0.67</b>	-0.2	0.53	1								
Mg	<b>0.67</b>	-0.39	0.38	0.62	1							
Na	<b>0.85</b>	-0.09	0.29	0.32	0.48	1						
K	<b>0.93</b>	-0.04	0.58	0.6	0.49	0.8	1					
HCO <sub>3</sub>	<b>0.87</b>	0.02	<b>0.67</b>	<b>0.76</b>	0.48	0.56	<b>0.87</b>	1				
Cl	<b>0.82</b>	0.07	0.31	0.36	0.45	<b>0.76</b>	<b>0.77</b>	0.57	1			
SO <sub>4</sub>	0.43	0.27	0.56	0.36	0.26	0.22	0.28	0.44	0.31	1		
NO <sub>3</sub>	0.34	-0.28	-0.1	-0.17	0.44	<b>0.63</b>	0.22	-0.14	0.48	-0.08	1	
SiO <sub>2</sub>	0.08	-0.34	0.24	<b>0.59</b>	0.46	-0.22	-0.12	0.18	-0.21	0.37	-0.26	1

Factor analysis was used to identify the underlying factors influencing the groundwater chemistry (Table 3). Three factors were extracted with 84.96% of total data variability (TDV).

Factor 1 was represented by Na, Cl, Ca, K, NO<sub>3</sub> and HCO<sub>3</sub>, indicating leaching of secondary salts. The interaction between these ions is explained by the strong correlations seen in Table 3. The presence of K and NO<sub>3</sub> indicates



**Figure 4** | Dendrogram of HCA, including all water samples. The water samples are linked into clusters on the x-axis and the linkage distance is plotted on the y-axis.

**Table 3** | Factor analysis for the chemical composition of groundwater

	Component		
	Factor 1	Factor 2	Factor 3
Na	.721	-.029	.609
K	.941	.108	.218
Mg	.287	.672	.594
Ca	.545	.749	-.052
Cl	.765	-.004	.480
SO <sub>4</sub>	.383	.485	-.072
NO <sub>3</sub>	.052	-.139	.976
HCO <sub>3</sub>	.890	.374	-.107
SiO <sub>2</sub>	-.200	.944	-.108

Extraction method: principal component analysis. Rotation method: varimax with Kaiser normalization.

anthropogenic inputs from agriculture and poor sanitation practices. A good correlation between HCO<sub>3</sub> and Ca could reflect the signatures of natural water recharge and rock-water interaction. Surface water charged with atmospheric and biogenic CO<sub>2</sub> infiltrates into the subsurface and aggressively attacks aluminosilicates, including feldspars and micas, liberating cations such as Ca into the water and leaving residues of clay minerals. This leads to a rise in the pH and HCO<sub>3</sub> concentration of the water (Prasanna *et al.* 2010). However, the study by Oyebog *et al.* (2012) on the hydrogeochemical characteristics of some bottled waters in Cameroon stated that in the case of volcano-sedimentary terrains, the high concentration on HCO<sub>3</sub> and Ca in groundwater could suggest that carbonate mineral weathering might be playing a key role in the hydrochemical process.



Factor 2 was represented by Mg, Ca and SiO<sub>2</sub>, indicating natural weathering processes; while Factor 3 was represented by Na, Mg, Ca and NO<sub>3</sub>, indicating anthropogenic inputs.

### Hydrochemical facies

Four hydrochemical facies were identified based on the major ion chemistry of the groundwater. The Na–K–Cl facies is dominant; it constitutes about 52% of the water samples, and 62% of group 1 samples fall in this facies. Na + K–HCO<sub>3</sub> facies represents 20% of water types which include group 2 and group 3; Ca/Mg–HCO<sub>3</sub> facies represents 17%, with the rainwater sample falling in this category and Ca/Mg–SO<sub>4</sub>/Cl facies represents 11% of the samples; the Nsimi water sample falls in this group. The Nsimi groundwater is regarded as recharged water in areas where groundwater is at its early stage of geochemical evolution (Braun *et al.* 2005).

### Mechanisms controlling groundwater chemistry

#### Geochemical processes

The Na/Cl molar ratios vary from 6.62 to 0.48, with 88% of samples having a molar ratio greater than 1. Meybeck (1987) used Na/Cl molar ratios to study silicate weathering reactions and showed that a Na/Cl molar ratio > 1 reflects Na<sup>+</sup> released from silicate (feldspar) weathering by the process of ion exchange, whereas ratio < 1 implies that another source is contributing chloride to the groundwater. In addition, Rogers (1989) stated that where silicate mineral weathering is the dominant controlling process, the concentrations of the major ions would be relatively low. Therefore 80% of sodium in the groundwater could be derived from silicate weathering. This process may also be the dominant factor controlling the groundwater chemistry in the area, as indicated by the low concentrations of major elements (Table 1). Further, Gibrilla *et al.* (2010) found that in addition to weathering, oxidation and dissolution of minerals were the major geochemical processes governing the groundwater evolution in the Densu river basin in Ghana.

Gibbs (1970) suggested two diagrams to illustrate the natural mechanisms controlling groundwater chemistry. In these diagrams, the dominant anions (Cl/(Cl + HCO<sub>3</sub>))

and cations (Na + K)/(Na + K + Ca) are plotted against the total dissolved solids in order to evaluate the geochemical processes (rock dominance, evaporation dominance or precipitation dominance).

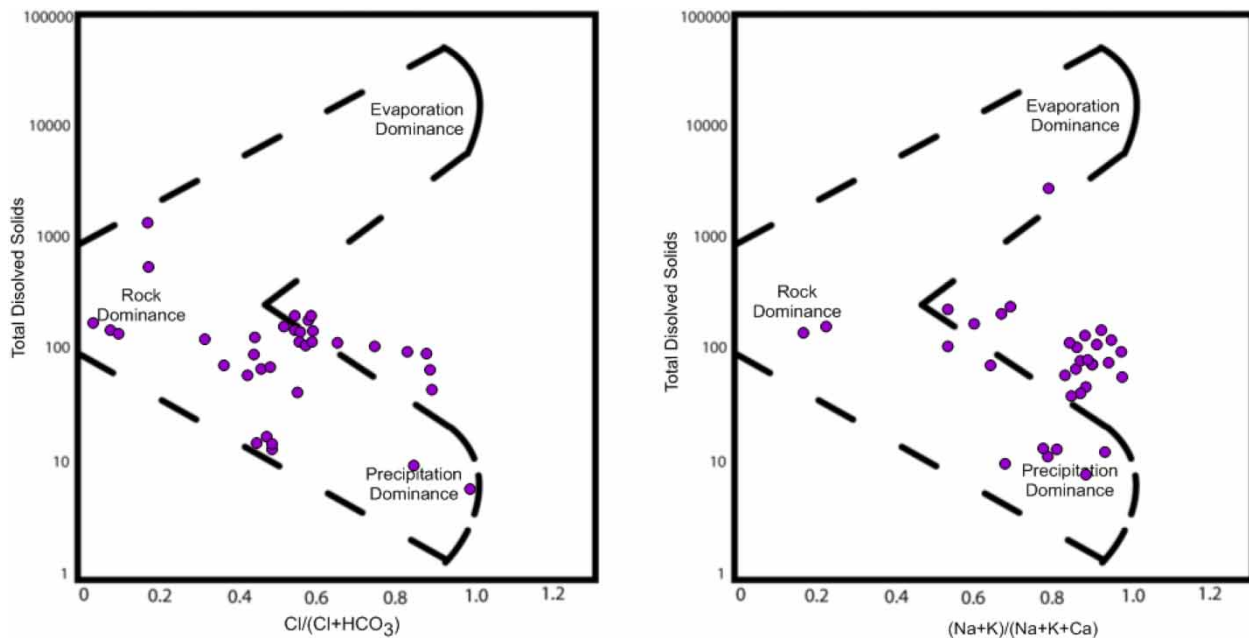
Gibbs ratio I (anions) values vary between 0.01 and 0.96, with an average of 0.68, while Gibbs ratio II (cations) values vary from 0.26 to 0.97, with an average of 0.70. Figure 5 shows that most of the water points are located in the rock dominance zone, which indicates water–rock interaction.

Gibbs diagrams showed that the geochemical evolution of groundwater in the present study site is controlled by two factors: water–rock interactions and precipitation (not very pronounced).

#### Water–rock interaction

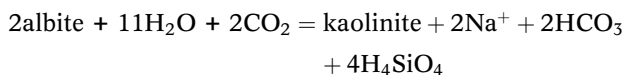
Interaction between groundwater and the surface of the surrounding host rocks is believed to be one of the processes responsible for the observed chemical characteristics of groundwater in the Yaoundé area. Figure 6 shows the plots of SIs against total dissolved solids for all the investigated groundwater. In the following discussion, we have assumed that an SI within the range of ±0.5 units from zero indicates the equilibrium state. The SI of quartz varies from –0.44 to +0.89. About 92% of samples were in equilibrium state while 8% (3 boreholes) were over-saturated with respect to quartz. The SI of chalcedony ranges from –0.86 to +0.89; 25% of water samples were under-saturated state and 75% were in equilibrium with respect to chalcedony. The SI of amorphous silica ranges from –1.69 to –0.38; 94% of samples were under-saturated and 6% were in equilibrium with respect to amorphous silica (Figure 6(a)). The saturation state of these groundwaters with respect to quartz confirms the presence of siliceous mineral in this environment and their inability to dissolve more of this mineral.

On the other hand, the SIs for carbonate (Figure 6(b)) and sulphate (Figure 6(c)) minerals show that all the samples are under-saturated with respect to calcite (0.19 > SI > –6.47), dolomite (0.16 > SI > –12.32), aragonite (0.04 > SI > –6.62), anhydrite (–2.74 > SI > –6.46) and gypsum (–2.51 > SI > –6.24), suggesting that these carbonate and sulphate mineral phases are absent in the corresponding host rock.



**Figure 5** | Gibbs plots showing geochemical processes in the groundwater of the study area.

In [Figure 7](#), most of the groundwaters fall within the stability field of quartz and kaolinite. This observations suggest that groundwaters are contained in a mineral environment mainly made up of aluminosilicates. It is therefore possible that the chemical composition of this groundwater may be attributed to equilibrium between primary aluminosilicate minerals and kaolinite, as described by the following reaction equation for albite:



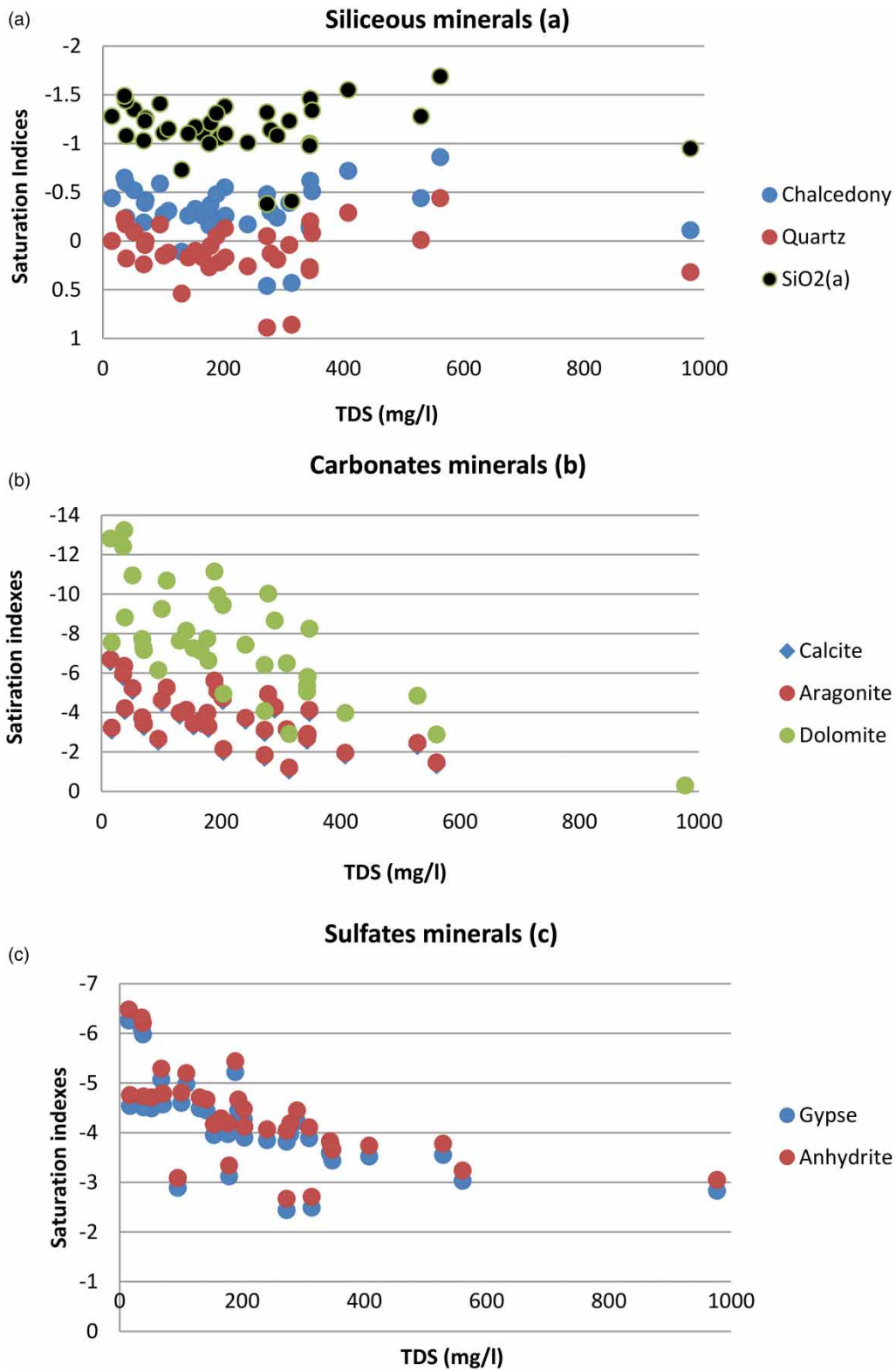
This process generally enriches the groundwater with  $\text{HCO}_3^-$  and rock-forming elements such as  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$  and dissolved  $\text{SiO}_2$ , and results in the formation of Na- $\text{HCO}_3^-$  groundwater type ([Hudson & Golding 1997](#)). The observed heterogeneity in  $\text{Na}^+$  and  $\text{Ca}^{2+}$  concentrations for these groundwater samples may, however, reflect local mineralogical changes in the groundwater reservoir and/or variations in the weathering rate with regard to the production rate of carbon dioxide ([Ngnotué \*et al.\* 2012](#); and [Kuitcha \*et al.\* 2013](#)).

## Evaporation

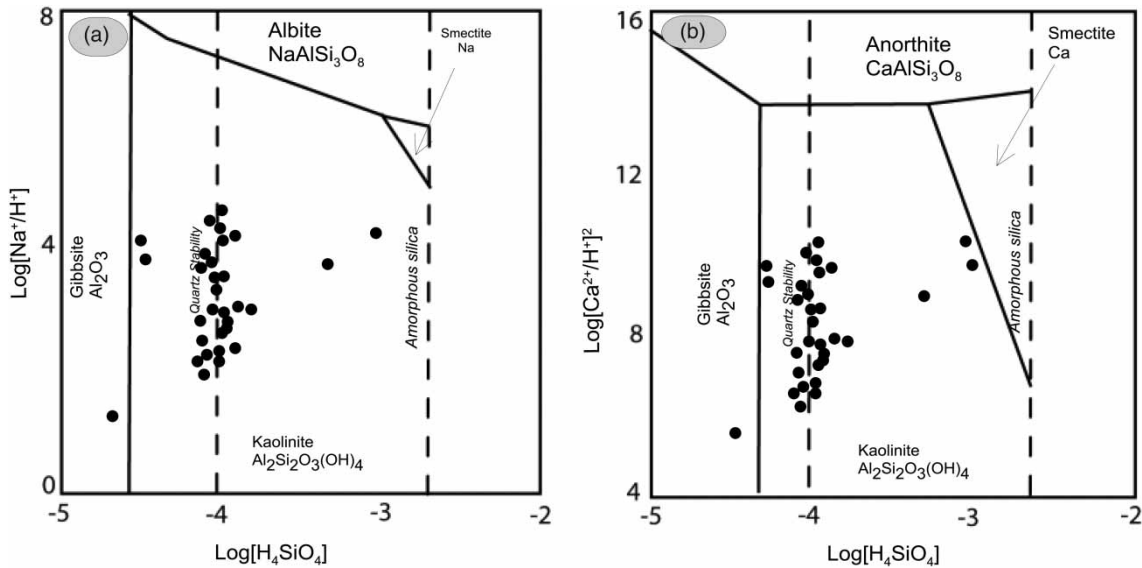
The Na/Cl ratio varies widely (from 0.48 to 6.62) in the groundwater of this area ([Figure 8](#)) and shows a sloping trend, which indicates that evaporation is not an important process in the study area. Assuming that no mineral species are being precipitated, concentration by evaporation would leave the Na/Cl ratio unchanged. The plot of Na/Cl versus EC would therefore produce a horizontal line ([Rajmohan & Elango 2004](#)). The slight increase of Na in groundwater indicates that silicate weathering, rather than evaporation, is likely to be a major source of groundwater mineralization.

## Origin of recharge and groundwater flow mechanisms

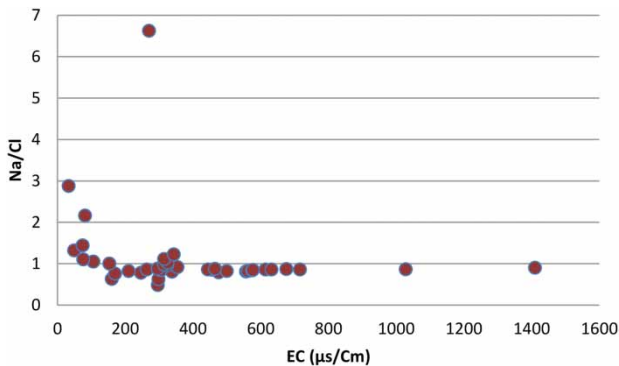
The  $^{18}\text{O}$  and  $^2\text{H}$  content for all the investigated groundwaters were plotted in [Figure 9](#), together with the global meteoric water line ( $^2\text{H} = 8^{18}\text{O} + 10$ ) defined by [Craig \(1961\)](#). The distribution of groundwater shows that all samples are located high and close to the meteoric water line. Isotopic analyses in [Table 4](#) also reveal that the oxygen-18 of groundwater ( $^{18}\text{O} = -2.96\text{‰}$  VSMOW) is close to the rainfall value ( $^{18}\text{O} = -2.47\text{‰}$  VSMOW), indicating that groundwater is recharged by rainwater derived



**Figure 6** | Plots of saturation indices with respect to some siliceous, carbonate and phosphate minerals, as computed with WATEQF against total dissolved solids.



**Figure 7** | Stability diagrams for some minerals in the systems Na–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–H<sub>2</sub>O (a) and CaO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–H<sub>2</sub>O (b) at 25 °C.



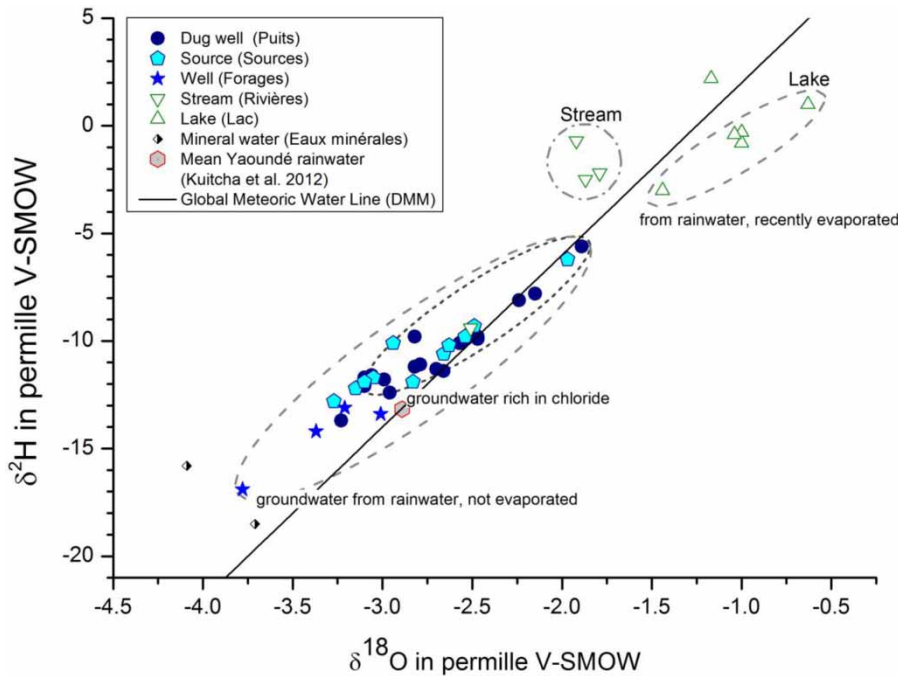
**Figure 8** | Relation between Na/Cl versus EC showing a slight increase of Na in some groundwater samples.

from direct infiltration of local precipitation without evaporation. This corroborates the geochemical results and supports the findings of *Ako et al. (2012)* and *Kuitcha et al. (2013)* in the coastal and crystalline regions of Cameroon, respectively. However, this situation is variable because in the coastal region of Ghana, *Adomako et al. (2011)* realized that the meteoric water recharging the groundwater system had undergone some degree of evaporation.

One of the postulates of this study is that the degree of water–rock interaction is dependent on the residence time of groundwater (*Wang et al. 2015*). According to *Fouépé Takounjou (2012)*, groundwater flows from elevated and

less permeable areas towards the more permeable zones through piston or preferential flow. The recharge areas of aquifers are located on higher elevations zones, corresponding to the upstream area of the watershed, around Bastos area (*Figure 1*). Therefore, groundwater flows from Bastos neighbourhood towards Ngoa-Ekele. The high hydraulic conductive values of  $5 \times 10^{-5}$  m/s, added to an average vertical hydraulic gradient of 0.17, lead to a groundwater flow rate of 0.37 m/d (*Fouépé Takounjou et al. 2013*). Considering that the water table occurs at depths between 12 and 20 m with respect to the soil surface, the results imply that it will take 32 to 54 days for rainwater to reach the water table.

The slow horizontal circulation of groundwater ensures a longer residence time for the interaction between water and the surrounding rock material. Some authors (*Denning et al. 1992*; *Jiang et al. 2012*) have stated that chemical concentrations in groundwater are governed by the residence time of water in the soil/bedrock. This supports the theory that residence time controls the concentration of chemicals produced by mineral weathering (*Hudson & Golding 1997*; *Wang et al. 2015*). Considering the position of well 1 (W1) located upstream of the Mfoundi river basin, and well 25 (W25) located downstream of the watershed (*Figure 3(a)*), an increase in the chemical constituents is observed along the flow line. For example, EC increases from 25 µs/cm at



**Figure 9** |  $^{18}\text{O}$  versus  $^2\text{H}$  plot for groundwater from the Yaoundé area according to the common types of water points. Surface water and mean Yaoundé rainwater are given for comparison.

**Table 4** | Comparisons between  $^{18}\text{O}$  and  $^2\text{H}$  in the groundwater and rainwater

Water point	$^{18}\text{O}$	$^2\text{H}$
Average rainwater ( $n = 18$ ) (Kuitcha <i>et al.</i> 2012)	-2,47	-8,06
Groundwater (borehole, well and spring) ( $n = 35$ )	-2,96	-11,93

W1 (Bastos) to a value of  $476 \mu\text{s}/\text{cm}$  at W25 (Ngoa-Ekele). Also, sodium and nitrate values from upstream to downstream increase from 7.6 and 18.8 mg/l at W1 to 54.5 and 112 mg/l at W25, respectively (Figure 3(a)). The directions of these trends are generally consistent with increases in the specific conductance of the samples, which reflect increased rock–water interaction. The pH of water samples also increased along these trends and confirms the silicate hydrolysis reactions, which are related to the rock–water interaction processes. To sum up, based on the hydrochemistry and recharge mechanisms of groundwater, we found that groundwater in elevated areas is young, less mineralized and corresponding to an earlier stage of groundwater evolution, compared to groundwater in the discharge areas.

## CONCLUSION

Hydrogeochemical investigations revealed that groundwater chemistry in Yaoundé is influenced by geochemical processes and anthropogenic inputs. Based on the geochemical results, three components were extracted to identify the factors influencing the groundwater chemistry. Factor 1 indicated leaching of secondary salts, Factor 2 represented natural weathering processes while Factor 3 indicated anthropogenic inputs.

The Gibbs diagram indicated that the geochemical evolution of groundwater is mainly controlled by water–rock interactions while the saturation index analysis pointed to the presence of siliceous mineral and the absence of carbonate and sulphate mineral phases in the corresponding host rock.

The correlation of  $\text{HCO}_3^-$  content with major cations suggested the leaching of the host granite rocks by  $\text{CO}_2$ -charged recharging waters, indicating the geogenic origin of groundwater chemistry in the study area. However, high nitrate and chloride concentrations detected in groundwater samples also illustrated that water chemistry is affected by

land-use activities, especially sewage effluents, application of chemical fertilizers and household solid wastes.

Isotopic data revealed that groundwater is recharged by rainwater derived from direct infiltration of local precipitation without evaporation. The recharging water generally flows from high topographic areas to lower topographic areas by the piston flow mechanism.

Based on the hydrochemistry and recharge mechanisms of groundwater, it can be concluded that groundwater in elevated areas is young, less mineralized and corresponds to an earlier stage of groundwater evolution, compared to groundwater in the discharge areas.

Finally, data produced in the framework of this study can be used to raise awareness on the origin and amount of chemical elements in groundwater. Authors who are interested in geochemistry and health could investigate whether the water quality meets the requirements of bottled mineral water or they could link the effect of the concentration of these elements on the health of people in this environment.

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