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Hydrogeochemical characteristics of some Cameroon bottled waters, investigated by multivariate statistical analyses

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ABSTRACT

In this study, 8 bottled water brands sold in Cameroon were analyzed for 76 elements/parameters by ICP-MS, IC, titration and mass spectrometric methods. This was to investigate the geochemical characteristics of the bottled waters in order to identify the main hydro geochemical processes controlling their chemical content. A comparison of the element concentrations and the legal limits for both bottled and tap water (Cameroon, EU, US EPA, WHO) shows that Aluminium concentration in three brands is above the lower guideline value set by EPA with very high lead concentration (6.4 μg/l) in one brand. Various water quality classification systems were used in to characterize the different bottled water types. Piper diagram was used to establish that dominant chemical types of the bottled water brands are Ca–HCO_3, Ca–Mg–HCO_3, Ca–Na–Mg–HCO_3, Na–HCO_3 and Na–Mg–HCO_3. Application of R-Mode factor analysis to the data set allowed the determination of the possible relationship between the distribution of individual elements and lithology or other surface enrichment phenomena. In particular waters draining through volcanic rocks are enriched in elements such as As, B, Br^-, Cl^-, Cs, F, K, Li, Na, NO_3^-, PO_4^{3-}, Rb, Sc, SiO_2, Sr, Te, Ti, and V. One of the three R-Mode factor analysis associations, recognized as being representative of elements analyzed shows high nitrate and Pb loadings along with As, PO_4^{3-} and Zn. The latter association probably reflects a sign of anthropogenic contribution in the volcano-sedimentary aquifers of the study area. Q-Mode hierarchical cluster analysis established four major groups amongst the bottled water brands. Stable water isotopes (δD and δO^{18}) established that the recharge origin of the bottled waters and other groundwaters of the study area is meteoric.

1. Introduction

Although there's abundant water on the earth's surface, freshwater is scarce and resources are unevenly distributed over the world, with much of the water located far from human populations (Güler and Alpaslan, 2009; Petraccia et al., 2006). The amount of water present on the earth's surface is estimated at ~1.41 bn km^3, of which only ~2.5% is fresh water (Wolff, 1999). Most of this potable water comes from springs and groundwater. About 99% of the fresh water is stored as groundwater. Water from these sources is used for various purposes among which is bottling/packaging in food grade containers for human consumption. Bottled/packaged waters form an increasingly utilized source of drinking water in both developed and developing countries.

Bottled water could be one of the sources for supply of toxic trace metals (Alien et al., 1989; Cicchella et al., 2010; Ikem et al., 2002; Krachler and Shotyk, 2009; Misund et al., 1999); heavy metals (Karamanis et al., 2007) and radionuclide (Dueñas et al., 1997; Rangel et al., 2002; Wallner et al., 2008). While the dissolved radionuclide and minerals allegedly instil medicinal benefits in persons who drink the water, consumption contributes to the body intake of these constituents (Kitto et al., 2005).

The abundance of toxic chemicals, radionuclide, nitrites and nitrates in drinking water may cause adverse effects on the human health such as cancer, other human body malfunctions and chronic illnesses (Ikem et al., 2002). There may be considerable risk to humans, especially children exposed to bottled water containing toxic elements and microbiological entities.

In Cameroon, surface water resources such as rivers and streams together with groundwater (boreholes and springs) are the main sources of water supplies in urban and rural areas. Water from these sources is usually collected, treated and distributed to the populations by the Cameroon Water Utilities (CAMWATER). CAMWATER is present in only 35% of cities and towns (Tanawa et al., 2002). Eighty two percent of the urban population and 42% of the rural population are covered in terms of water supply with 23% of households having direct access

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to drinking water (WHO, 2000). In 2006, 70% of the population had access to safe drinking water. The coverage in urban centres was 88%, significantly higher than the 47% in rural areas (WHO/UNICEF, 2008). Of Cameroon's 300 urban centres with 5000 inhabitants or more, however, only 98 have water supply networks. Moreover, rapid urbanization in smaller towns has often rendered existing infrastructure inadequate, with frequent service interruptions (Ako et al., 2010).

Thus, many people still rely on bottled water for safety purposes, for infants (for formula preparation, drinking water and reconstitution of food), health reasons and for drinking water. Even travellers into the country are usually advised to drink bottled water for safety purposes. Though the production of bottled started in 1999, it was only until 2007 that consumption got to its peak due to public conception about municipal water supplies. Between 1999 and 2009, 15 bottled water companies in Cameroon produced about 52,380,000 bottles of water and about 1,080,000 l of water in sachets mostly from groundwater sources (MINEE, 2010). The increasing number of companies engaged in bottling and distributing bottled water for sale by retailers in Cameroon raises questions about the differences between the water supplied by these companies, both when compared to each other and when compared to tap water.

The main purpose of the present study, in which 8 samples of bottled water brands sold in Cameroon were analyzed for 41 elements/parameters, was to investigate the geochemical characteristics of the bottled waters in order to identify the main hydrogeochemical processes and influences controlling their chemical content. A further objective of the study was to determine the natural variation of the element concentrations in bottled water and tap water. This paper compares and describes several water classification methods and illustrates the differences in the requirements that have to be met by bottled water and tap water. The action levels established by Cameroonian, European Union and US EPA regulations for selected parameters are compared.

2. Materials and methods

2.1. Geologic and hydrogeologic setting

Cameroon is located between latitudes 2°N and 13°N and longitude 4°E and 16°E (Fig. 1). It is crossed diagonally by the Cameroon Volcanic Line (CVL) a chain of Tertiary to Recent volcanic peaks and grabens that extend from the Atlantic Island of Pagalu to the Bui and Adamawa plateaus in Nigeria and Cameroon respectively (Fitton and Dunlop, 1985; Fitton et al., 1983). These volcanics constitute a fifth of the major rock types in the national territory and constitute the principal water shade while the remainder 4/5 is made up of sedimentary rocks of the Douala, Mamfe, Rio del Ray, Kribi–Campo and the Logoon Birini Basins and metamorphic rocks of the southern plateau.

The study area lies on the south eastern foot slopes of Mount Cameroon and within parts of the Littoral Region (Fig. 1). It is bounded by the Atlantic Ocean to the South and West, to the North by active Mt Cameroon and by the Douala basin to the East. Six of the bottling plants are located on the volcanics along the CVL whereas two are present within the Douala sedimentary Basin characterized by a flat landscape with mean altitude of 30 m above sea level. The Mount Cameroon section of the study area is characterised by the presence of alkali basaltic rocks (basalt, basanite, pricrite, haiwiiate, picrobasalts mugeaurite) and rich in calcium, iron and magnesium silicate mineral such as olivine, pyroxene, and calcic plagioclase. This section is made up of thick soil sequence formed from the weathering of the rocks that make up the different zone. As a result, this region is very fertile and useful for subsistence and industrial agricultural (banana, palm, rubber and tea plantation). It rich water resources have added to the additional influx of human actives (Lambi and Kometa, 2009). The Douala Basin consists of sandstones (quartz), limestone, shales, clay, and conglomerates. Douala, economic capital of Cameroon, is located within the Douala sedimentary basin which is also characterised by high industrial activities. The Douala sedimentary basin possesses vast water resources, in the form of groundwater and stream or surface water. The two bottling plants found in this basin extract ground water from boreholes while those found on volcanic along the CVL obtain water from springs and boreholes.

2.2. Sampling and analytical methods

This study is limited to eight popular bottling plants located across the South West and Littoral Regions of Cameroon. Water samples for analysis were purchased at bottling plants or from distribution vans. The locations of different domestic bottled water plants are shown in Fig. 1.

Eight bottled mineral water brands were used for this study. To keep the brand names anonymous, the water samples were given alphabetical code from A to H and this convention used throughout the text. Out of the 8 brands, 6 brands had all eight important parameters (Ca^{2+}, Na^{+}, Mg^{2+}, K^{+}, Cl^{-}, SO_4^{2-}, HCO_3^{-} and NO_3^{-}) on their bottle labels. Two brands had the pH of the water on their labels. One brand (C) reported generalized information on trace elements, heavy metals and method of treatment on it labels. Three brands (A, B, and C) are tapped from natural springs and five (D, E, F, G and H) from boreholes.

Physico-chemical parameters of the samples were measured immediately after sample collection. pH was measured using a PL 150 Thermo Russel Model pH meter. Electrical conductivity (EC) was measured using a Hanna Instruments H 19811 pH-EC-TDS meter. Temperature (T) of the water samples was measured using a Casella London 28237c Mercury Thermometer.

Analysis for anions was done at the Institute for Research in Agricultural Development (IRAD) Ekona laboratory. Bicarbonate (HCO_3^{-}) and Chloride (Cl^{-}) concentrations were determined by titration. The other anions (SO_4^{2-}, NO_3^{-} and PO_4^{3-}) and Ammonium ion (NH_4^{+}) were analysed by colorimetric/tubidimetric methods using a Perkin-Elmer Spectrophotometer 295E. The analysis of major and trace elements was carried by Acme Analytical Laboratory in Canada, an internationally accredited laboratory. Samples were acidified to pH <2 as soon as possible after collection with environmental grade (ultra pure) nitric acid. The acidified samples were then placed in sterile HDPE containers of 50 ml capacity, (which had carefully be rinsed several times with the sample water) and kept for seven days to dissolve any absorbed or precipitated metals. Major and trace metals were determined by enhanced ICP-ES/ICP-MS. Samples were analyzed directly by ICP-MS to determine trace to ultra-trace concentrations of elements and by ICP-ES to confirm higher concentrations. Samples were analyzed for 69 metals (Ag, Al, As, Au, B, Ba, Be, Bi, Br, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, In, K, La, Li, Lu, Mg, Mn, Mo,Na, Nb, Nd, Ni, P, Pb, Pr, Pt, Rb, Re, Rh, Ru, Sb, Sc, Se, Si, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn and Zr). The analytical quality control included analysis of blanks and duplicate analysis of samples and standards reference materials to provide a measure of background noise, accuracy and precision. For comparison, a tap water sample from the study area was also analysed for its major and trace element contents. The general public believes that bottled water is safer and healthier than tap water.

Stable isotopic contents (oxygen-18 (δO^{18}) and deuterium (δD)) analysis was done for three of the brands (A, E and G) and other groundwater sources in the vicinity of the study area. This analysis was done at the Isotope Hydrology Laboratory of Kumamoto University-Japan. A mass spectrometer (Thermo Quest Finnigen H/Device for hydrogen isotope and Finnigen mat Delta S for oxygen isotope)

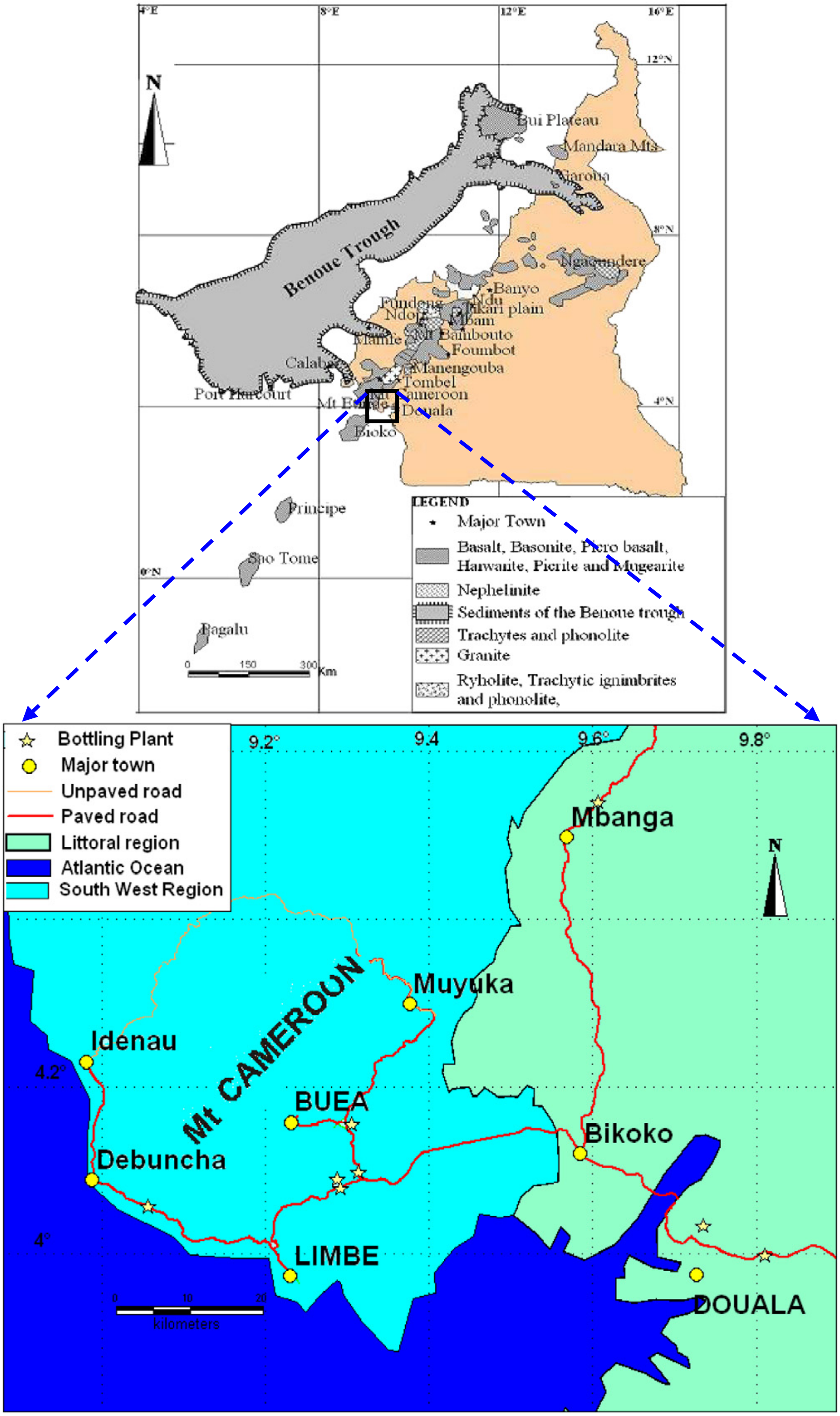

Fig. 1. Location of bottling plants on volcanics along the CVL and sedimentary rocks of the Douala Basin. Inset is a Map of the CVL modified after Déruelle et al., 1987; Fitton et al., 1983; Marzoli et al., 1999.

was used. Stable isotope results were expressed with respect to Vienna Standard Mean Ocean Water (VSMOW) in δ units (‰):

$$\delta^{18}O = \{[(^{18}O/^{16}O)_{sample} - (^{18}O/^{16}O)_{standard}]/(^{18}O/^{16}O)_{standard}\} \times 10^3 (‰) \quad (1)$$

$$\delta D = \{[(D/H)_{sample} - (D/H)_{standard}]/(D/H)_{standard}\} \times 10^3 (‰) \quad (2)$$

where, oxygen and hydrogen isotope ratios are expressed by $\delta^{18}O$ and δD, respectively, $(^{18}O/^{16}O)_{sample}$ or $(D/H)_{sample}$ is the isotopic ratio in the sample water, $(^{18}O/^{16}O)_{standard}$ or $(D/H)_{standard}$ is isotopic ratio in standard mean ocean water. Reproducibilities for δD and $\delta^{18}O$ were ±1 and ±0.1‰, respectively.

Bottled water brands were also characterized by means of univariate and multivariate analysis techniques using analytical chemical parameters. Censored values (values that were below detection limit) were replaced by 0.55 times the lower detection limit (Sanford et al., 1993). Elements with a high proportion of data below the detection limit (>50%) were not accepted in the analysis. This reduced the number of parameters from 76 to 42 parameters. Correlation Analysis, Factor Analysis (FA) and Hierarchical Cluster Analysis (HCA) were used to evaluate variation and similarities amongst the various bottled water brands.

Factor Analysis was used to examine the relationships among the variables. Unlike Pearson correlation coefficient that establishes the relationship between two variables, factor analysis seeks to bring out the relationship existing between multiple variables coexisting together. Principal component analysis (PCA) reduces the number of variables in the data matrix, to select the most discriminating parameters and to investigate the overall variation of data. This method can be performed only if correlation among variables in the data matrix occurs (Lewi, 1992). The resulting data for all parameters were log-normal and had to be log-transformed to meet the requirements of optimal R-Mode factor analysis (Güler et al., 2002). Principal component analysis linearly combines two or more correlated variables into one variable. A normalized varimax rotation of the factors and scores was performed to find the rotation that will maximize variability on the factors, minimize it everywhere else, and maintain the factors orthogonal to each other (Meloun et al., 1992). This helps reduce the contribution of variables with minor significance. Each factor is orthogonal, or uncorrelated, to the others and measures, or explains, in a successively decreasing residual manner, data variability not accounted for by the previous factors (Woocay and Walton, 2008). Each factor is an eigenvector with one component, or load, per original variable, and the amount of variation explained by a factor is an eigenvalue (which is the sum of the squares of the component of each factor loading). The number of PCs extracted (to explain the underlying data structure) was defined by using the "Kaiser criterion" (Kaiser, 1960) where only the PCs with eigenvalues greater than unity are retained.

Hierarchical cluster analysis was used to see if the brand could be grouped into distinct groups. 11 variables (Ca^{2+}, Cl^-, EC, HCO_3^-, K^+, Mg^{2+}, Na^+ NO_3^-, pH, SiO_2 and SO_4^{2-}) were used for this analysis. The assumptions of cluster analysis techniques are equal variance and normal distribution of the variables. Thus all variables were log transformed and standardized. In this way, each variable has equal weight in the statistical analyses (Güler et al., 2002) without which calculation of the Euclidean distance will be influenced most severely by the parameters with the largest in their distribution if the raw data are used (Güler et al., 2002; Yidana, 2010). Classification of samples according to their parameters is termed Q-mode classification. Comparisons based on multiple parameters from different samples are made and the sample grouped according to their similarity to each other. The results are then presented as a dendogram with the numbers of groups selected based on visual examination of the dendogram.

3. Results and discussion

3.1. Hydrogeochemical classification of bottled water brands

Different hydrochemical classification systems have been used to classify water types (Matthess, 1994; Matthess and Ubell, 1983). Some classification systems were used to identify the chemical similarities/differences between bottled water brands. The studied bottled water brands were classified according to (i) total dissolved solids (TDS) (ii) water hardness (iii) dominant ions.

3.1.1. Classification based on TDS and characterizing cations and anions

The European Union (EU) mineral water directive (Van der Aa, 2003) was used to classify the water. The criteria for the chemical composition of mineral water according to the EU mineral water directives are given below (Table 1). The criteria show a distinction based TDS and a further specification based on some characterizing cations and anions.

Table 2 shows classification of bottled waters for this study in accordance with EU mineral water directive. All the 8 brands fall in the class "low mineral concentration" (with TDS between 50 and 500 mg/l). Based on the characterizing cations and anions, 87.5% of the bottled water brands fall in class suitable for low sodium diets. This class consists of brands: A, B, C, D, E, F and H with Na^+ concentration<20 mg/l. Brand G with sodium concentration of 43.94 mg/l does not belong to this class. None of the bottled water falls in the other classes of cation and anion.

3.1.2. Classification based on water hardness

Total hardness in water is caused by dissolved calcium and to a lesser extent magnesium. Water hardness was determined for all bottled water brands using the equation (Crittenden et al. (2005):

$$\text{Total hardness} = 2.5[Ca^{2+}] + 4.1[Mg^{2+}]$$

where $[Ca^{2+}]$ = calcium concentration in mg/l

$[Mg^{2+}]$ = magnesium concentration in mg/l

According to Crittenden et al. (2005) water is typically classified as follows (Table 3):

Bottled water brands for this study were classified based on total hardness as shown in Table 4. Five of the brands with hardness between 100 and 150 mg/l are considered hard, two brands with hardness between 50 and 100 mg/l are moderately hard and one brand with hardness between 0 and 50 mg/l is considered soft water.

Table 1
Mineral water classification based on EU directive.

Mineral water type	Criterion
Very low mineral concentration	Mineral content (TDS)<50 mg/l
Low mineral concentration	TDS 50–500 mg/l
Intermediate mineral concentration	TDS 500–1500 mg/l
High mineral concentration	TDS>1500 mg/l
Containing bicarbonate	Bicarbonate>600 mg/l
Containing sulfate	Sulfate>200 mg/l
Containing chloride	Chloride>200 mg/l
Containing calcium	Calcium>150 mg/l
Containing magnesium	Magnesium>50 mg/l
Containing iron	Bivalent iron>1 mg/l
Containing sodium	Sodium>200 mg/l
Suitable for low sodium diets	Sodium<20 mg/l

Table 2
Classification of mineral water brands in the various classes in accordance with the EU mineral water directive.

Class	Brand
Very low mineral concentration	none
Low mineral concentration	A, B, C, D, E, F, G, H
Intermediate mineral concentration	none
High mineral concentration	none
Suitable for low sodium diets	A, B, C, D, E, F, H

3.1.3. Classification based on dominant ions

Bottled water brands were classified using bar chart, pie diagrams and Piper's diagram. Both systems of classification are based on dominant ions. The bar chart, pie charts and Piper's diagram were drawn using the values in Table 5.

The bar chart (Fig. 2) shows composition of major ion in each brand in meq/l. The height of the bar chart is proportional to the total dissolved solids content of the water. Brand G has the highest TDS. Pie diagrams (Fig. 3) show relative proportion of major ion in each brand in % meq/l. In general magnesium and bicarbonate represent the dominant cation and anion respectively.

As seen in Fig. 4, the Piper's trilinear diagram displays the relative concentrations of the major cations and anions on two separate triangles together with a central diamond plot where the points from the linear plots are projected. Employing the water classification scheme of Davis and De Wiest (1966), the samples are classified into five water types (Table 6). The dominance of $Mg^{2+}$and HCO_3^- is also evident from the result of the Piper's diagram.

3.2. Water chemistry and natural variation of elements

The chemical content of bottled water is determined by the composition of the rocks it is abstracted from. Similar types of rock may lead to different types of mineral water. The chemical content depends on the availability of mineralizing agents, such as CO_2 concentration, redox conditions and the type of adsorption complexes (Birke et al., 2010).

Results of measured physico-chemical parameter of the bottled water brands are presented in Table 7 together with MAC set by CAC (1981); MAV for ISMC (2001), GV recommended by WHO (2008) and MCL set by EPA (2009). The ranges of values for the physico-chemical parameters are: 90–410μS/cm for electrical conductivity (EC) with a median of 294.7 μS/cm; 6.34–7.91 for pH with a median of 7.28; 26.7–27.0 °C for temperature with a median of 26.8 °C; and 85–355 mg/l for total dissolved solid (TDS) with a median of 255 mg/l. Electrical conductivity showed the highest spread (i.e. standard deviation at 1 sigma, SD) whereas temperature had the lowest SD. There is a great variation between the EC values of the bottled water brands, which is related to the total dissolved solids (TDS) content, the origin of the water, and the treatment or purification method applied during bottling process. Electrical conductivity in water is usually used as a measure of ionic concentration. The low EC of brand D is due to its low ionic concentration.

Minimum pH is observed in brand E and maximum pH in brand B. The acidic nature of brand E could be resulting from organic acids in the soil as well from atmospheric sources. Since the brands were labelled as Natural Mineral Water, this might mean no carbon dioxide was present in the water. A pH value of 6.5 is the minimum recommended by ISMC, WHO and EPA, brand E therefore falls short of this recommendation. Electrical conductivity and TDS values are below MAV for ISMC. No standard is provided for temperature of water.

Table 3
Water classes based on hardness.

Total Hardness, mg /l as $CaCO_3$	Water Class
0-50	Soft
50-100	Moderately hard
100-150	Hard
Above 150	Very hard

Table 4
Classification of the bottled water brands based on total hardness.

Brand Code	Total Hardness(mg/l)	Water class
A	117.68	Hard
B	107.33	Hard
C	78.43	Moderately hard
D	2.99	Soft
E	123.50	Hard
F	149.75	Hard
G	117.39	Hard
H	78.74	Moderately hard

In this study, chemical analysis for 74 parameters was done for the 8 bottled water brands.The results show that the bottled water brands are quite different in characteristics. Observed variations in the chemical constituents might be resulting from the origins of the water, residence time of the water in the rocks, atmospheric conditions and purification/treatment process employed by the manufacturers. Table 8 gives the analytical results of major constituents found in these brands together with the corresponding standards/guideline values used in this study. The concentration range for the major constituents (in mg/l) is: 0.67–57.90 for Ca^{2+} with a median of 19.15; 0.19–9.18 for K^+ with a median of 4.46; 0.32–18.54 for Mg^{2+} with a median of 11.86; 1.45–43.94 for Na^+ with a median of 10.64; 2–12 for Cl^- with a median of 4; 67.71–229.97 for HCO_3^- with a median of 165.92; 0–1.58 for NO_3^- with a median of 0.03; 2–11 for SO_4^{2-} with a median of 4; and 2.01–29.15 for SiO_2 with a median of 14.25.

Higher concentration of Ca^{2+} is observed in brand F from sedimentary terrain because of abundance of limestone. Calcium readily dissolved from rocks rich in calcium minerals, clay minerals, sulfates and other carbonate rocks especially limestone and gypsum. The exception was seen with brand D also from a sedimentary zone but with an extremely low Ca^{2+} content (0.67 mg/l). Brand D actually has the lowest concentration of all major constituents with exception of Na^+.

The exceptionally low concentration of Ca^{2+} but high Na^+ concentration in brand D may be an indication that the water is sourced from waters which have undergone natural softening by cation exchange. Most commonly, clays will exchange Na^+ if available for both Ca^{2+} and Mg^{2+}. Another possibility of this exceptional concentration might be due to method of processing. Sodium chloride can be used in ion exchange so Na^+ ions will exchange with Ca^{2+} and Mg^{2+} ions. Higher Mg^{2+} concentration is generally observed among water from volcanic terrain (brands A, B, C, E, G and H). This is due to presence of magnesium-rich minerals such as olivine and pyroxene. The

Table 5
Water analysis results of major constituents for bottled waters in Cameroon.

Brand code	Elemental concentration (meq/l)					
	Ca^{2+}	Mg^{2+}	$Na^+ + K^+$	HCO_3^-	SO_4^{2-}	$Cl^- + NO_3^-$
A	1.14	1.23	0.90	3.11	0.10	0.06
B	0.98	1.18	0.55	2.67	0.08	0.12
C	0.79	0.79	0.53	2.13	0.04	0.09
D	0.03	0.03	0.44	1.11	0.04	0.06
E	1.20	1.29	0.29	3.37	0.06	0.06
F	2.90	0.10	0.59	2.77	0.10	0.28
G	0.83	1.55	2.15	3.77	0.23	0.34
H	0.93	0.65	0.3	1.37	0.06	0.18

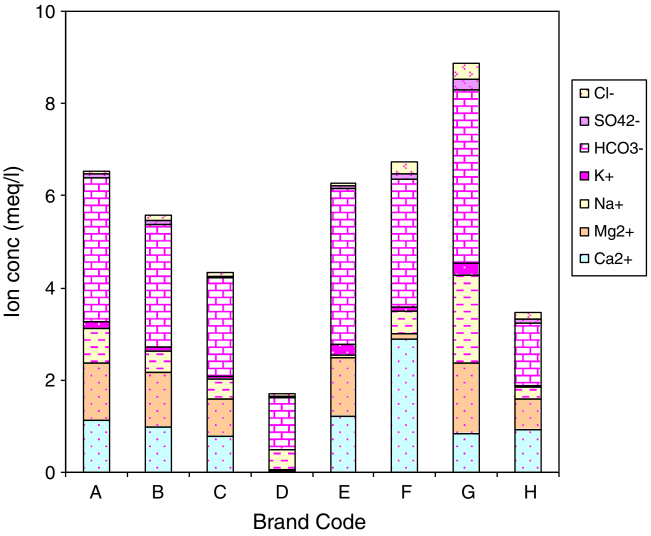

Fig. 2. Bar diagram showing the proportion of ionic constituents in each bottled water brand.

concentration of Ca^{2+} was greater than Mg^{2+} in all brands except brand G. This exception might be due to exchangeable sodium. This brand has Na concentration between ~27 and 42 units higher than the others. Primary source of sodium in natural water is from release of soluble products during the weathering of plagioclase feldspars. No health-based guideline value is proposed for Ca^{2+}, K^{+}, $Mg^{2+}$and Na^{+} in drinking water by WHO due to contrasting views on health impacts of these elements. Each country set its own standards based on its local circumstances. Maximum concentrations of these major cations are generally lower than ISMC.

Chloride (Cl^{-}) in water comes from sea water entrapped in sediments, solution of halite or chloride contributed by rain. Bicarbonate (HCO_3^{-}) is the most dominant anion probably because of the reaction of atmospheric and soil carbon dioxide with water and from carbonate dissolution. High nitrate (NO_3^{-}) concentration (1.58 mg/l) in brand F relative to the others may be resulting from erosion of natural deposits or most likely from industrial and agricultural wastes. But this value is below standards/guideline set for nitrate in drinking water. Sulfate (SO_4^{2-}) in natural water originates from oxidation of sulphide ores, gypsum and anhydrite. Silicon (Si) is the second most abundant element in the Earth's crust after oxygen. Higher concentration of silica (SiO_2) in brands from the volcanic area is due abundance of silicate mineral. Lower concentration in the sedimentary area is probably due to abundance of quartz and clay mineral which attests to slow rate of solution of sources silica. The higher sodium, chloride and sulfate content in brand G relative to the others might be resulting from release of soluble products during weathering of plagioclase feldspars, salt water intrusion or chloride-rich rainwater. Brand E from volcanic area tends to have lowest concentration of Na^{+} with respect to the others. No standards or guideline value is proposed for HCO_3^{-} and SiO_2 in drinking water. The standards/guideline values provided for Cl^{-} and SO_4^{2-} are based on consumer's acceptability of taste and concentrations were below these values.

In terms of chemical quality, the tap water sample is richer in mineral salts than one bottled water brand (Brand D) putting in question the general notion that bottled waters are generally richer in mineral salts than tap water.

3.3. Concentration of trace elements

The analytical results of trace constituents are presented in Table 9 together with MAC set by CAC (1981); MAV for ISMC (2001), GV recommended by WHO (2008) and MCL set by EPA (2009). The concentration range for the trace constituents(in μg/l) is: 0.11-1.05 for Ag with a median of 0.15; 30–121 for Al with a median of 49; 5–37 for B with a median of 15; 6.73–90.99 for Ba with a median of 18.12; 9–90 for Br with a median of 18; 0.07–0.17 for Cd with a median of 0.11; 0.28–0.98 for Ce with median of 0.37; 0.03–0.83 for Co with a median of 0.08; 3.1–9.0 for Cr with a median of 4.5; 0.9–12.5 for Cu with a median of 1.4; <10–52 for Fe with a median of 13; <0.1–0.1 for Hg with a median of 0.1; 0.11–6.51 for La with a median of 0.19; <0.1–5.4 for Li with a median of 0.3; 1.11–51.00 for Mn with a median of 12.61; 0.1–4.4 for Mo with a median of 0.8; 0.05–2.93 for Nd with a median of 0.07; 0.4–2.3 for Ni with a median of 0.9; 76–258 for P with a median of 132; 1.2–6.4 for Pb with a median of 2.2; 0.49–23.59 for Rb with a median of 6.85; <0.01–0.03 for Rh with a median of 0.02; 0.06–0.78 for Sb with a median of 0.44; 0.15–0.55 for Sn with a median of 0.21; 4.67–222.38 for Sr with a median of 104.23; <0.02–2.25 for U with a median of 0.03; 0.2–22.8 for V with a median of 4.9; <0.02–1.09 for W with a median of 0.14; 0.01–0.11 for Y with a median 0.02; 14.4–89.0 for Zn with a median of 23.9 and 0.13–0.84 for Zr with a median of 0.23.

Trace elements such as arsenic (As), gold (Au), beryllium (Be), europium (Eu), holmium (Ho), indium (In), lutetium (Lu), palladium (Pd), platinum (Pt), rhenium (Re), ruthenium (Ru), scandium (Sc), samarium (Sm), terbium (Tb), tellurium (Te), thulium (Tm) and ytterbium (Yb) were non-detectable in any of the bottled sample. Ammonia (NH_4^{-}) was also not detected in any of the samples. Trace elements such as bromide (Br), bismuth(Bi), cerium (Ce), cobalt (Co), caesium (Cs), dysprosium (Dy), erbium (Er), gallium (Ga), gadolinium (Gd), germanium (Ge), lanthanum (La), lithium (Li), niobium (Nb), neodymium (Nd), phosphorus (P), phosphate (PO_4^{2-}), praseodymium (Pr), rubidium (Rb), rhodium (Rh), tin (Sn), tantalum (Ta), thorium (Th), titanium (Ti), vanadium (V), tungsten (W), yttrium (Y) and zirconium (Zr) for which no standards or guideline values are provided by CAC, ISMC, WHO and EPA were detected in some of these bottled water brands. Dysprosium was detected only in brand F, Er in brand A, Ga in brand A, Gd in brands E and F, Ge in brand A, Nb in brands A, D and F, Pr detected in brands A and F, PO_4^{3-} was detected in brands A, B and G, Se in brands F and G, Ta in brand A, Th in brands A and B and Ti in brand B. Thallium (Tl) was detected in brands E and F and the concentration in these brands are below standard value provided by EPA.

Higher concentration of Ag is observed in brands A, B and C with respect to others. Silver salts are used to maintain the bacterial quality of drinking water and this might be a reason for the observed concentrations in these brands. Maximum Ag concentration is below EPA standard value. Thorium and Bi in brands A and B may be originating from natural deposit or radioactive decay of uranium and its daughter products. Brand E tend to have very high Al, Ba and Li concentrations relative to others from same area. This might be due to relative mobility of these elements at lower pH. Aluminium tends to be the third most abundant element on the Earth's crust. Another possible source of Al might be from piping systems. The primary Ba mineral is barite but it often occurs in the lattices of some common silicates like feldspars. Ba is not very mobile (in the secondary environment) but it can be mobilized by acidic waters. Lithium is preferentially leached during the weathering of silicate rocks. K-feldspars, amphiboles and clay minerals have the most important contents of Li. Aluminium concentrations in brands D, E and F (from sedimentary terrain) are above the EPA lower secondary standard limit of 50 μg/l.

The highest concentration of boron (B), bromide (Br), manganese (Mn) and zinc (Zn) was found in sample F from sedimentary areas. Boron is found naturally in groundwater. Boron compounds are also used in the manufacture of glass, soaps and detergents and as flame retardants. Boron from these sources may be a contributing source of the high boron content in brand F. However, maximum concentration of B (37 μg/l) is quite below the guideline value (500 μg/l) set by WHO (2008). Zinc (Zn) is generally found in ores as sulphide, but it is

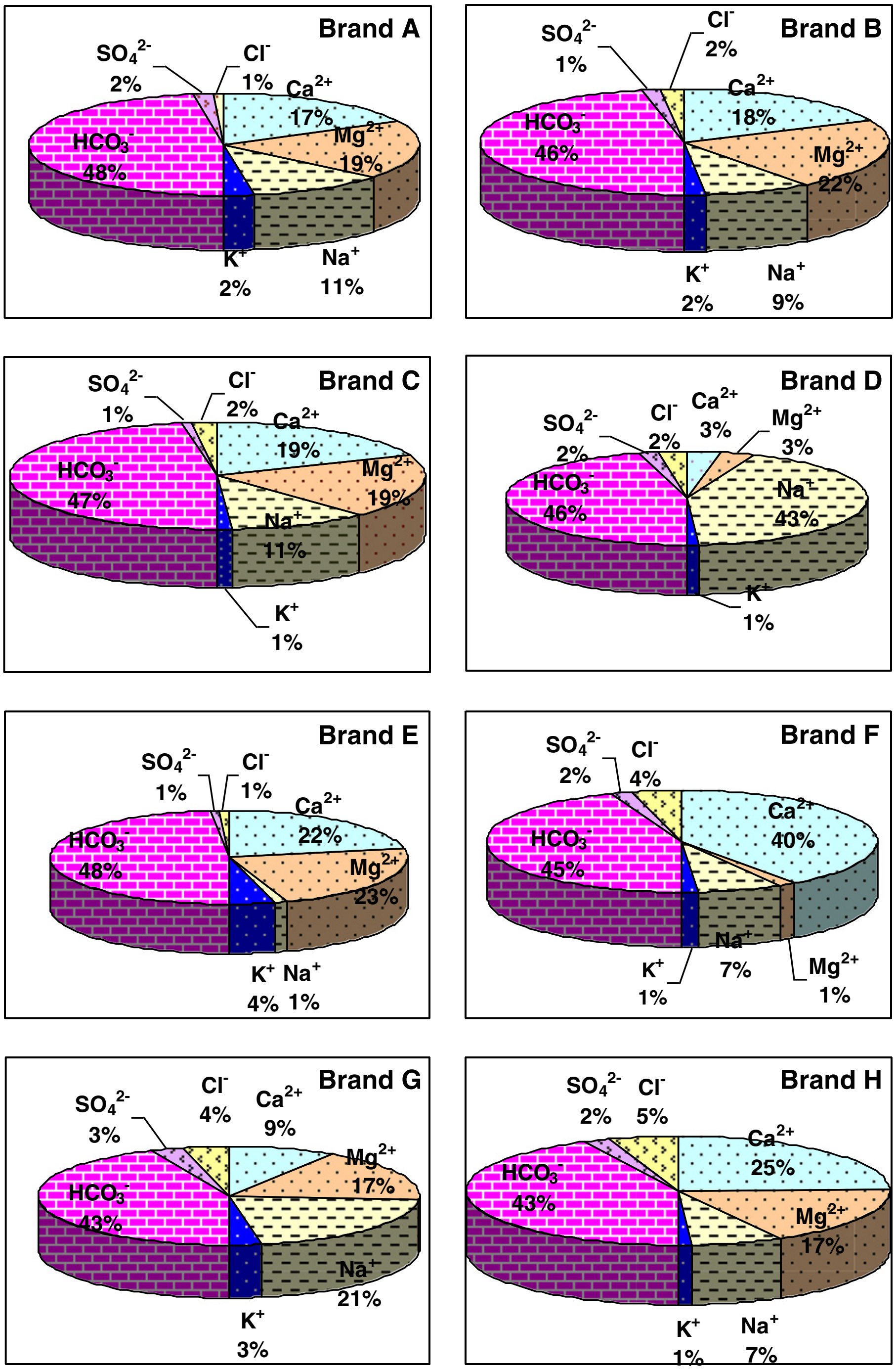

Fig. 3. Pie diagrams showing relative concentrations of the major cations and anions in each bottled water brand.

rather widespread in all the most important rock types. Maximum Zn concentration is below guideline value based on taste. Manganese is a natural occurring element in the Earth's crust occurring with iron. It is also use in disinfection. Maximum Mn concentration is above guideline value provided by EPA.

Copper (Cu) concentration in brand D is higher with respects to the others. This might be originating from corrosion of plumbing systems or erosion from natural deposits. Germanium (Ge) in brand A may be from leaching of Ge catalyst used in production of PET. Maximum manganese concentration (in brand F) is above guideline value provided by EPA. With the exception of brand D (also in PET bottle), higher antimony (Sb) concentrations are observed in water from PET bottles than from HDPE bottle (brand B). The presence of Sb in these bottled water brands may include additional Sb leaching from the bottle material. However, concentration in these brands was below standard values. Iron is one of the most abundant metals in the Earth's crust. Sources of iron include weathering of pyroxenes minerals in volcanic areas and oxides, carbonates, and sulfides or iron clay minerals in sandstone areas. Maximum Fe concentration is below the value for standards used in Cameroon and by EPA (2009). These values are set based on acceptability factors (taste and color). No health-based guideline value is proposed for iron in drinking

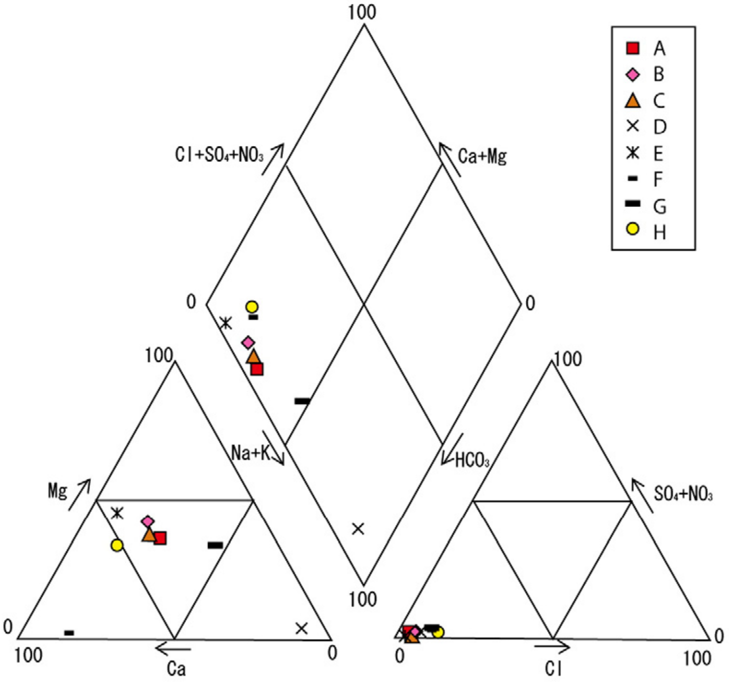

Fig. 4. Piper's diagram of 8 bottled water brands showing the water types.

water. Lanthanum concentration in brand A is about 6 units higher than concentration in the other brands. Lanthanum is one of the most reactive of the rare-earth metals and reacts with water to form the hydroxide. No standard is provided for Bi, La and Th.

Phosphorus (P), rubidium (Rb) and strontium (Sr) concentrations are higher in brands from the volcanic area. Secondary environmental weathering of the common minerals is the main source of Rb. Higher Sr content in water from volcanic terrain may include additional Sr-90 which is a fission product of U-235 or other fissile nuclide. No health baseline has been set for P, Rb and Sr in drinking water by the standard used in this study. All brands in which mercury was detected had same mercury concentration suggesting the mercury might be originating from erosion of natural deposits. Concentrations of Pb in brands A and D are about 4.5 and 4 times higher than concentration found in the other brands from same geologic terrain respectively. This higher concentration might be originating from lead pipes used to tap water from source to the bottling plants. Higher concentration of Pb than U in all the samples except for brand G may be an indication of radioactive decay of U. Lead (Pb) is the daughter of radioactive decay of U. Maximum Hg and Pb concentrations are below standards. Molybdenum (Mo) and vanadium (V) occur naturally in soils and may be entrained into water due to its mobility during weathering. U is release in water in these areas through erosion of natural deposits. Difference in the concentration of U may be due to U greater mobility under oxidizing conditions and it present in very varying concentrations in rocks.

Table 6
Five water types resulting from classification using Piper's diagram.

Water type	Brands code
Ca–HCO_3	F
Ca–Mg–HCO_3	E, H
Ca–Na–Mg–HCO_3	A, B, C
Na–HCO_3	D
Na–Mg–HCO_3	G

3.4. Recharge origin of bottled waters and other groundwaters in the study area

The results of the isotopic measurement of stable isotope of oxygen (O^{18}) and hydrogen (D) for three of the brands, springs and

Table 7
Physico-chemical parameters for the 8 bottled water brands and their comparison to the CAC (1981), ISMC[a] (2001), WHO (2008) and US EPA (2009) standards/guideline values.

Brand code	EC[b] (μS/cm)	pH	Temperature (°C)	TDS[c] (mg/l)
A	334.0	7.34	26.9	273
B	275.1	7.91	26.8	249
C	216.1	7.50	26.9	193
D	90.0	7.81	27.0	85
E	314.3	**6.34[d]**	26.8	268
F	292.9	6.73	26.8	261
G	410.0	7.26	26.8	355
H	171.9	7.34	26.7	151
Range	90–410.0	6.34–7.91	26.7–27.0	85–355
Median	294.7	7.28	26.8	255
Mean	275.5	7.28	26.8	229
SD	111.0	0.52	0.1	84
CAC (1981) MAC[e]	–	–	–	–
ISMC (2001) MAV[f]	<400	>6.5 and <9	–	1500
WHO (2008) GV[g]	–	6.5–8.0	–	–
EPA (2009) MCL[h]	–	6.5–8.5[i]	–	500[i]

[a] International standard for mineral water used in Cameroon.
[b] Electrical conductivity.
[c] Total dissolved solid, μS/cm = microseconds per centimetre.
[d] Bold numbers indicate value below limits of standards.
[e] Maximum allowable concentration.
[f] Maximum allowable value, mg/l.
[g] Guideline value.
[h] Maximum contaminant level; dashes indicate no standard is available for the parameter.
[i] Secondary maximum contaminant level (non-enforceable guideline) established by EPA to regulate contaminants that may cause cosmetic or aesthetic effects in drinking water.

Table 8
Analytical results of major constituents of the 8 bottled water brands and their comparison to the CAC (1981), ISMC (2001), WHO (2008) and US EPA (2009) standards/ guideline values.

Brand code	Major Constituents(mg/l) Ca^{2+}	K^+	Mg^{2+}	Na^+	Cl^-	HCO_3^-	NO_3^-	SO_4^{2-}	SiO_2
A	22.88	6.15	14.75	17.09	2	189.71	0	5	15.41
B	19.66	3.59	14.19	10.87	4	162.87	0.20	4	29.15
C	15.76	2.14	9.52	10.41	3	129.93	0.08	2	19.75
D	0.67	0.19	0.32	9.92	2	67.71	0	2	2.01
E	24.08	9.04	15.44	1.45	2	205.57	0	3	7.18
F	57.90	3.86	1.22	11.26	9	168.97	1.58	5	2.12
G	16.55	9.18	18.54	43.94	12	229.97	0	11	14.08
H	18.64	1.56	7.84	5.95	6	83.57	0.50	3	24.30
Tap water	13.49	8.88	7.26	18.74	3	180.00	0	4	20.83
Range	0.67–57.9 0	0.19–3.86	0.32–18.54	1.45–43.94	2–12	67.71–229.97	0–1.58	2–11	2.02–29.15
Median	19.15	3.73	11.86	10.64	3.5	165.92	0.03	3.5	14.74
Mean	22.02	4.46	10.23	13.86	5	154.54	0.24	4	14.25
SD	16.19	3.36	6.74	12.96	4	57.14	0.55	3	10.01
CAC (1981) MAC^1	–	–	–	–	–	–	50	–	–
ISMC^2 (2001) MAV^3	<100	12	50	150	200	–	50	250	–
WHO (2008) GVs^5	–	–	–	–	250$^{T4\ 4}$	–	50	250$^{T\ 3}$	–
EPA (2009) MCL^7	–	–	–	–	250$^{g6\ 55}$	–	10	250^g	–

$^{1)}$Maximum allowable concentration; $^{2)}$ international standard used for mineral water in Cameroon; $^{3)}$ maximum allowable value, mg/l; $^{3)}$ guideline value based on taste; $^{4)}$ guideline value based on taste; $^{5)}$ guideline value; $^{6)}$ secondary maximum contaminant level (non-enforceable guideline) established by EPA to regulate contaminants that may cause cosmetic or aesthetic effects in drinking water; $^{7)}$ maximum contaminant level; dashes indicate no standard is available for the parameter.

groundwater in the vicinity of bottling plants are shown in Table 10 below.

In order to determine the recharge origin of the bottled waters and other groundwater sources in the vicinity of the bottling plants, a scatter plot of δD against δO^{18} (delta diagram) was drawn (Fig. 5) containing the Global Meteoric Water line (GMWL) given by (GMWL, $\delta D = 8 \times \delta O^{18} + 10$) (Craig, 1961).The scatter plot for our data set gives a line of equation, $\delta D = 10.2 \times \delta O^{18} + 19.1$ which is very close to that of the GMWL. This indicates that the origin of recharge water for the bottled water and other groundwaters in the study area is meteoric water i.e. water that has been recently involved in atmospheric circulation. They were recharged with some evaporation before or during the infiltration process. The slope (10.2‰) and deuterium excess (19.1‰) of the scatter plot are higher than those of the Global Meteoric Water Line ($\partial^2 H = 10\partial^{18} O + 10$) indicating that the heavy isotope contents of the rains giving rise to the ground waters have been altered by evaporation during recharge. In a hydrological system where moisture recycling through evaporation and/or evapo-transpiation play a significant role in the water cycle, higher d-excess values (>10‰) have been reported (Gat and Carmi, 1970; Matsui et al., 1983).

The points of the bottled water brands reflect the humidity and temperature of the surrounding environment during precipitation. Brand G which is from a higher elevation region with high humidity above 85 atm is depleted in stable water isotopes and plot on the lowest part of the GMWL. Brand A from a lower elevation region with humidity<85 atm plots is richer in heavier stable isotopes heavier than Brand G and plot on the mid portion of GMWL. Brand E from a very a low altitude area with a warmer climatic condition plots on the upper portion of the GMWL compared to other brands.

3.5. Multivariate statistical analysis

3.5.1. Correlation analysis

Pearson correlation coefficients (r) were calculated for all possible pairs of variables to establish the correlation existing between them and this is presented in Table 11. Bold implies correlation is significant at the 0.05 level (2-tailed). r values show that there exist a very high positive correlation($r > 0.80$) between Ca^{2+} and Cl^-, Ca^{2+} and NO_3^-, Cl^- and NO_3^-, HCO_3^- and K^+, HCO_3^- and Na^+, K^+ and Na^+, Mg^{2+} and SiO_2; high positive correlation(>0.5) between HCO_3^- and Ca^{2+}, K^+ and Ca^{2+}, SO_4^{2-} and Ca^{2+}, Cl^- and SO_4^{2-}, HCO_3^- and SO_4^{2-}, K^+ and SO_4^{2-}, NO_3^- and SO_4^{2-}. High correlations between the variable pairs are also desired for the application of Factor analysis (FA) and Hierarchical cluster analysis (HCA).

3.5.2. Factor analysis

Factor analysis was used to examine the relationships among the variables. Principal component extraction reduces the number of variables in the data matrix, to select the most discriminating parameters and to investigate the overall variation of data. Table 12 presents the eigenvalues, the percentage of variance, the cumulative eigenvalue and the cumulative percentage of variance associated with each other. Three components resulted from the application of the Kaiser criterion (Kaiser, 1960) which explains the total variation (100%) in the data set. Table 13 shows the loading of vaimax rotated component matrix for three-component model.

Principal component 1(Ag, –Al, –B, –Ba, –Br, –Ca^{2+}, –Cl^-, –Cu, La, Mg^{2+}, Mo, Nd, –NO_3^-, P, pH, Rb, Rh, –Sb, SiO_2, Sn, Sr, V, –Y, –Zn, –Zr (−Co, Cr and Fe)) is responsible for the largest part (38.52%) of the total variance of the data set. This component has a very strong positive correlation with Ag, Mg, Mo, P, pH, Rb, Rh and Sn; a strong correlation with La, Nd, SiO_2, Sr and V; and a moderate correlation with Cr and Fe. It is characterized by very high trace element content reflecting the control of certain lithologies. Lithological control is due to the interaction of water with volcanic rocks. Very high positive factor loading for pH (0.97) implies this component represents the major process controlling concentrations of the element in solution. Increase pH tends to increase concentration of Ag, La, Mg^{2+}, Mo, Nd, P, Rb, Rh, Sb, SiO_2, Sn, Sr, V, Cr and Fe in solution. Increase pH tends to decrease solubility of calcium carbonate and increase solubility of silicates mineral.

Principal component 2 (Al, B, Ca^{2+}, Ce, –Co, Cr, Cs, EC, –Fe, HCO_3^-, K^+, La, Li, Na^+, Nd, –SiO_2, –Sr, U, –V, –W, Y, Zr (Ba, Sn,)) accounts for 34.44% of the total variance. It is characterized by very high positive factor loading (>0.80) for B, Ce, Cr, Cs, EC, HCO_3^-, K^+, Na^+, and U; high positive factor loading value for Al, Ca^{2+}, La, Li, Nd, Y and Zr; and moderate loading for (Ba and Sn). This component reflects mostly the control of certain lithologies and mineralisation. It is characterized by high major ion (HCO_3^-, K^+, Na^+, and Ca^{2+}) content. The high factor loading value (0.86) for EC results from the high concentration of the major ions. Highly positive correlated value for K^+, HCO_3^-, and Na^+ is most likely related to weathering of silicate minerals. High factor HCO_3^- and moderate Ca^{2+} also suggests that

Table 9

Concentration of trace elements found in the 8 bottled water brands together with the MAC set by CAC (1981); MAV for ISMC (2001), GV recommended by WHO (2008) and MCL set by EPA (2009).

Trace elements (μg/l)

Brand code	Ag	Al	B	Ba	Br	Cd	Ce	Co	Cr	Cu	Fe	Hg	La	Li	Mn
A	1.05	50	15	24.12	10	0.07	0.98	0.04	9.0	1.3	<10	0.1	6.51	0.2	22.86
B	0.94	47	13	17.4	16	0.15	0.40	0.06	5.1	1.4	28	0.1	0.56	0.6	14.08
C	0.80	34	16	13.53	17	0.07	0.35	0.04	4.8	1.0	<10	<0.1	0.22	0.1	1.11
D	0.11	**52**[a]	6	6.73	18	0.1	0.29	0.1	3.6	12.5	14	<0.1	0.12	0.4	11.14
E	0.16	**121**[a]	5	90.99	9	0.09	0.38	0.21	4.3	0.9	15	<0.1	0.14	5.4	19.98
F	0.12	**96**[a]	37	67.94	90	0.14	0.40	0.14	4.4	2.1	<10	0.1	0.23	1.4	**51.00**[a]
G	0.13	30	23	15.88	52	0.17	0.28	0.03	4.5	1.0	12	<0.1	0.11	<0.1	1.55
H	0.13	36	8	18.83	29	0.11	0.30	0.83	3.1	2.0	52	<0.1	0.16	0.2	6.76
Tap water	0.25	**66**	6	6.00	14	0.11	0.38	0.04	4.6	5.1	29	<0.1	0.15	0.10	0.69
Range	0.11–1.05	30–121	5–37	6.73–90.99	9–90	0.07–0.17	0.28–0.98	0.03–0.83	3.1–9.0	0.9–12.5	<10–50	<0.1–0.1	0.11–6.51	<0.1–5.4	1.11–51.00
Median	0.15	49	14	18.12	18	0.11	0.37	0.08	4.5	1.4	13	0.1	0.19	0.3	12.61
Mean	0.43	58	15	31.93	30	0.11	0.42	0.18	4.9	2.8	17	0.1	1.01	1.0	16.06
SD	0.42	33	11	30.38	28	0.04	0.23	0.27	1.8	4.0	16	1.7E-17	2.23	1.8	16.17
CAC (1981) MAC	–	–	–	700	–	3	–	–	50	1000	–	1	–	–	400
ISMC (2001) MAV	–	200	–	–	–	5	–	–	–	–	200	1	–	–	–
WHO (2008) GVs	–	200	500	700	–	3	–	–	50	2000	–	6	–	–	400
EPA (2009) MCL	100[b]	50–200[b]	–	2000	–	5	–	–	100	1300[c]	300	2	–	–	50[c]

Brand code	Mo	Nd	Ni	P	Pb	Rb	Rh	Sb	Sn	Sr	U	V	W	Y	Zn	Zr
A	1.5	2.93	0.5	118	6.4	9.88	0.02	0.31	0.55	78.96	0.04	0.7	0.32	0.03	23.3	0.20
B	1.2	0.19	0.8	258	2.5	7.79	0.03	0.18	0.52	198.8	0.03	9	0.03	0.03	35.5	0.33
C	1.1	0.08	1.5	193	1.2	5.91	0.01	0.44	0.35	128.05	0.05	19.3	0.24	0.02	14.4	0.24
D	0.1	0.06	1.0	81	5.9	0.49	<0.01	0.06	0.17	4.67	<0.02	0.2	<0.02	0.01	24.5	0.13
E	0.1	0.05	2.3	146	1.5	16.66	0.01	0.44	0.21	48.26	<0.02	0.2	<0.02	0.02	18.2	0.64
F	0.2	0.11	0.8	76	2.1	4.93	<0.01	0.76	0.21	27.69	0.03	0.5	0.02	0.11	89	0.84
G	4.4	0.05	0.4	197	2.2	23.59	<0.01	0.78	0.15	125.04	2.25	22.8	0.30	0.02	22.1	0.15
H	0.5	0.06	0.9	107	1.9	5.09	<0.01	0.74	0.18	222.38	<0.02	11.6	1.09	0.02	40.8	0.21
Tap water	1.5	0.06	0.5	205	2.9	20.81	0.01	0.13	0.21	129.10	0.18	19.8	0.09	0.03	83.6	0.17
Range	0.1 −4.4	0.05 −2.93	0.4 −3	76 −258	1.2 −6.4	0.49 −23.59	<0.01 −0.03	0.06 −0.78	0.17 −0.55	4.67 −222.38	<0.02 −2.25	0.2 −22.8	<0.02 −1.09	0.02 0.11	14.4 −89	0.13 −0.84
Median	0.8	0.07	0.9	132	2.2	6.85	0.02	0.44	0.21	102.00	0.03	4.9	0.14	0.02	23.9	0.23
Mean	1.1	0.44	1.0	147	3.0	9.29	0.02	0.46	0.29	104.23	0.30	8.0	0.29	0.03	33.5	0.34
SD	1.4	1.01	0.6	64	2.0	7.43	0.01	0.28	0.16	78.78	0.77	9.2	0.41	0.03	24.1	0.26
CAC (1981) MAC[d]	–	–	20	–	10	–	–	5	–	–	–	–	–	–	–	–
ISMC (2001) MAV[e]	–	–	–	–	10	–	–	–	–	–	–	–	–	–	–	–
WHO (2008) GVs[f]	70	–	70	–	10	–	–	20	–	–	15	–	–	–	–	–
EPA (2009) MCL[g]	–	–	–	–	15	–	–	6	–	–	30	–	–	–	5000[b]	–

[a] Bold numbers indicate value exceeding limits of standards. Median, mean and standard deviation for Li and U were calculated using 0.55 times the minimum detection limit for samples with Li and U concentrations below detection limits.

[b] Secondary maximum contaminant level (non-enforceable guideline) established by EPA to regulate contaminants that may cause cosmetic or aesthetic effects in drinking water.

[c] Action level.

[d] Maximum allowable concentration.

[e] Maximum allowable value, μg/l = micrograms per litre.

[f] Guideline value.

[g] Maximum contaminant level; dashes indicate no standard is available for the parameter.

carbonate mineral weathering might be playing a role in the hydrochemistry and indicates water hardness. Lithological control reflects interaction with volcano-sedimentary lithologies.

Principal component 3 (Al, Ba, Ca^{2+}, Cd, Cl^{-}, Cu, Li, Mn, –Ni, NO$_3^{-}$, Pb, SO$_4^{2-}$, Y, Zn, (Br, Cs, Fe, K^{+}, La, –Mo, –U, V, –W, Zr)) accounts for 27.07% of the total variance. This factor is characterize by very high positive loading for Cd, Li, Mn, Pb, SO$_4^{2-}$ and Zn; high loading for Al, Ba, Ca^{2+}, Cl^{-}, Cu, V and Y and moderate loading for Br, Cs, Fe, K^{+}, La, Mo, U, W and Zr. This component is characterized by heavy metals (Al, Ba, Cd, Cu, Li, Mn, Ni, Pb, Y, Zn, Cs, La, U, V, W and Zr). The determinants of this component might include both contributions from the weathering of rocks and anthropogenic supplies to the aquifers. Very high SO$_4^{2-}$ along with high loading of Ca^{2+}, Cl^{-}, K^{+}, and NO$_3^{-}$, and moderate EC loading may indicate elemental increases from anthropogenic sources such as fertilizers, agricultural wastes, industrial runoff or sewage. Although K^{+} correlates with component 3, it has a very high loading with component 2 suggesting that the processes represented by component 2 have a greater effect on the concentration of K^{+} than do those represented by component 3. High Ca^{2+}and SO$_4^{2-}$ factor loading also suggest the dissolution of gypsum. Very high negative loading of Ni (-0.997) indicate strong negative relationship between Ni and the variables describing this factor.

3.5.3. Hierarchical cluster analysis

Hierarchical cluster analysis was used for searching the natural grouping (based on their similarities) among bottled waters from

Table 10
Stable isotope compositions of bottled water brands and other groundwaters in the study area.

Sample	Water source	δO^{18} (‰)	δD (‰)
A	Spring	−3.8	−17.6
E	Borehole	−3.1	−17.1
G	Borehole	−4.4	−25.9
Range		−4.4 to −3.1	−25.9 to −17.1
Median		−3.8	−17.6
Mean		−3.8	−20.2
SD		0.63	4.92
Sample 1	Spring	−3.9	−21.2
Sample 2	Borehole	−4.2	−23.4
Sample 3	Borehole	−3.8	−19.4
Sample 4	Spring	−3.2	−13.4

SD: standard deviation.

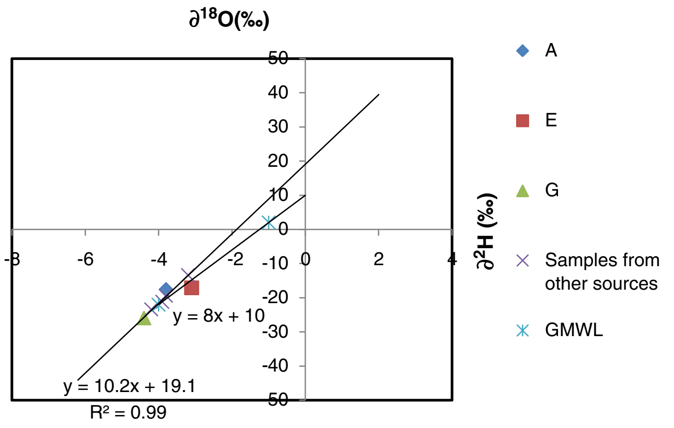

Fig. 5. A plot of δD (‰) against δO^{18} (‰) for 3 bottled water brands and samples from springs and boreholes around bottling plants together with the GMWL.

different sources. The bottled water brands were classified based on their major ion and physicochemical parameters (pH and EC).

The Ward's method was used to obtain hierarchical associations and the Euclidean distance was used as similarity measurement. Classification of samples according to their parameters is known as Q-mode classification. The result of the HCA is presented as a dendrogram (Fig. 6). Hierarchical cluster analysis is based on the visual inspection of the resulting dendrogram and interpretation is subjective. In this study, the "Phenon line" (Sneath and Sokal, 1973) was chosen at a linkage distance of 10. At this distance the groups that resulted were very clearly distinguishable in terms of their hydrochemical variables. This means that those clusters and samples under this line are recognized as being under the same group. The resulting dendrogram has four major groups based on a similarity of ten parameters. The first group (group 1) is composed of two subgroups: sub group 1 consisting of brand A, B, and C and subgroup two consisting H alone. The second group is comprised of brand E alone. The third group is composed of brand F and G; and the fourth group is consists of brand D alone.

The result of the cluster analysis shows that the most discriminating parameter (as seen in Table 14) used in grouping the samples is TDS. Mean TDS of group1 is 217 mg/l. That for group 2 is 268 mg/l. Group 3 has a mean TDS range of 308 mg/l and Group 4 has TDS of 85 mg/l.

HCA intends to classify hydrochemical observations so that the members of the resulting groups or subgroups are similar to each other and distinct from the other groups. This approach is commonly applied to water chemistry data in order to define groups of samples that have similar chemical and physical characteristics (Güler, 2007). The characteristics of the groups or sub-groups are not predetermined but can be obtained after the classification (Ayenew et al., 2009) and the members of one group or subgroup are similar to each and distinct from the other groups (Güler et al., 2002). Cluster analysis has been used to group samples into hydrochemical facies that can be correlated with location (Güler et al., 2002). In the result of cluster analysis in this study, brands A, B, C and H forming the first cluster are from the volcanic terrain. However, there is actually no clear cut for samples from sedimentary basin probably due to variation in the lithologies through which the water flow among others factors. In addition brand E and G from a volcanic area stand out separate from the others due to their mineral composition. Brand E tends to have very low sodium and brand G very high sodium concentration with respect to the others.

Table 11
Correlation among major constituents.

	Ca^{2+}	Cl^-	HCO_3^-	K^+	Mg^{2+}	Na^+	NO_3^-	SiO_2	SO_4^{2-}
Ca^{2+}	1.000								
Cl^-	**0.858**	1.000							
HCO_3^-	**0.515**	0.050	1.000						
K^+	**0.643**	0.268	**0.959**	1.000					
Mg^{2+}	**−0.947**	**−0.839**	−0.323	−0.410	1.000				
Na^+	0.376	−0.142	**0.964**	**0.850**	−0.241	1.000			
NO_3^-	**0.847**	**0.999**	0.050	0.277	**−0.816**	−0.150	1.000		
SiO_2	**−0.959**	**−0.764**	−0.479	**−0.540**	**0.984**	−0.409	**−0.740**	1.000	
SO_4^{2-}	**0.799**	**0.773**	**0.506**	**0.727**	**−0.582**	0.267	**0.793**	**−0.596**	1.000

Bold implies correlation is significant at the 0.05 level (2-tailed).

Table 12
Eigenvalues, percentage of variance, cumulative eigenvalue and cumulative percentage of variance for the factor analysis of the 8 bottled water brands.

Total variance explained									
Component	Initial eigenvalues			Extraction sums of squared loadings			Rotation sums of squared loadings		
	Total	% of variance	Cumulative %	Total	% of variance	Cumulative %	Total	% of variance	Cumulative %
1	21.938	52.233	52.233	21.938	52.233	52.233	15.996	38.086	38.086
2	13.870	33.025	85.258	13.870	33.025	85.258	14.393	34.270	72.356
3	6.192	14.742	100.000	6.192	14.742	100.000	11.611	27.644	100.000

Table 13
Loading for varimax rotated factor matrix of three-factor model explaining the total variance.

Elements	Component		
	1	2	3
Ag	0.866	0.324	– 0.380
Al	– 0.531	0.626	0.571
B	– 0.505	0.858	0.094
Ba	– 0.729	*0.442*	0.523
Br	– 0.877	0.254	*0.408*
Ca^{2+}	– 0.686	*0.517*	0.511
Cd	0.051	0.168	0.984
Ce	0.190	0.951	0.243
Cl^{-}	– 0.753	0.009	0.658
Co	– *0.464*	– 0.796	0.388
Cr	*0.476*	0.869	– 0.132
Cs	– 0.105	0.894	*0.436*
Cu	– 0.601	– 0.262	0.755
EC	– 0.265	0.861	*0.433*
Fe	0.396	– 0.789	*0.469*
HCO_{3}^{-}	0.146	0.962	0.230
K^{+}	0.084	0.867	*0.492*
La	0.773	*0.497*	0.394
Li	– 0.250	0.512	0.822
Mg^{2+}	0.874	– *0.404*	– 0.270
Mn	– 0.336	0.297	0.894
Mo	0.905	– 0.105	– 0.411
Na^{+}	0.168	0.985	– 0.036
Nd	0.622	0.726	0.294
Ni	0.072	0.010	– 0.997
NO_{3}^{-}	– 0.721	– 0.004	0.693
P	0.963	0.099	– 0.252
Pb	0.173	0.044	0.984
pH	0.969	– 0.212	– 0.127
Rb	0.963	0.245	0.112
Rh	0.946	0.306	0.108
SO_{4}^{2-}	– 0.226	0.343	0.912
Sb	– 0.950	– 0.288	– 0.120
SiO_{2}	0.791	– 0.559	– 0.248
Sn	0.887	*0.455*	– 0.086
Sr	0.722	– 0.676	– 0.147
U	0.219	0.855	– 0.471
V	0.660	– 0.523	– 0.539
W	– 0.069	– 0.885	– *0.460*
Y	– 0.569	0.646	0.509
Zn	– 0.543	0.140	0.828
Zr	– 0.503	0.721	*0.477*

Extraction method: Principal Component Analysis. Rotation method: Varimax with Kaiser Normalization. Rotation converged in 7 iterations. Very high factor's loadings (≥0.80) are in bold and underlined, high factor's loadings (≥0.50) are in bold and moderate (≥0.4) factor's loadings are in italics. Positive correlations are in red.

4. Conclusions

This study gives an insight into the diversity of bottled water sold in Cameroon as well as their limitations in terms of their physico-chemical and chemical quality and their stable water isotopic content. The results show that:

- The physico-chemical conditions of the waters are likely to favour the presence in solution of those elements forming soluble oxycomplexes in solution such as NO_3^-, PO_4^{3-}, V, Cr, Se, W, Mo, U, and As.
- Many elements, even the major ones, show very large natural variations; this is important information regarding the behavior of many elements for which few data are available so far. Their concentrations are independent from measured EC and likely reflect local geological settings. The bottled water brands belong to the bicarbonate (HCO_3^-) type of dominant Ca-Mg characteristics though, Na and Na–Mg dominant waters also exist.
- Trace elements such as Br, Bi, Ce, Co, Cs, Dy, Er, Ga, Gd, Ge, La, Li, Nb, Nd, P, Pr, Rb, Rh, Sn, Ta, Th, Ti, V, W, Y and Zr for which no standards or guideline values are provided by CAC, ISMC, WHO and EPA detected in these bottled water brands are difficult to evaluate. There is a need for recommendations of maximum values, and ometimes also for minimum values for these toxic elements.
- The occurrence of many elements can be directly related to aquifer lithology. In particular volcanic lithologies provide a clear and distinct hydrogeochemical signal in the groundwaters. As, B, Br—, Cl—, Cs, F, K, Li, Na, NO_3^-, PO_4^{3-}, Rb, Sc, SiO_2, Sr, Te, Ti, and V are enriched in waters draining through volcanic rocks compared to waters draining through other lithologies, in many cases with limited overlap among groups. Waters draining through sedimentary rocks do not display any distinct behavior and only show high median values for Al.
- Multivariate statistical analysis (Pearson correlation coefficients, Factor analysis and Hierarchical cluster analysis) clarified the complex multivariate relationships among the elements and parameters. Most of the extracted factors with their high loading of element associations have geological sources. The resulting dendrogram from the Hierarchical cluster analysis has four major groups based on a similarity of ten parameters.
- Stable water isotopes (δD and δO^{18}) have established that the recharge origin of the bottled waters and other groundwaters of the study area are meteoric with little or no evaporation during the recharge process.

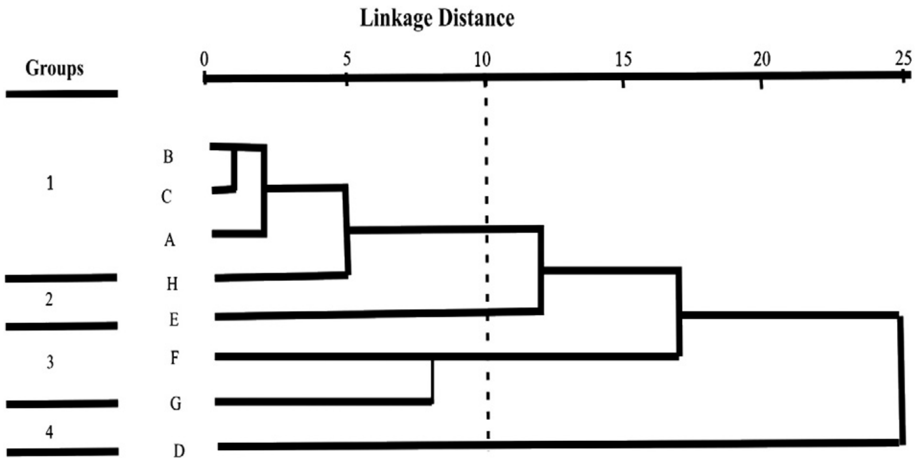

Fig. 6. Dendrogram from the HCA for the 8 bottled water samples using Ward Method. Each group indicates bottled water with similar physico-chemistry.

Table 14
Mean values of the physical and major chemical parameters in each HCA group.

Group	EC(μS/cm)	pH	Ca^{2+} (mg/l)	K^{+}	Mg^{2+}	Na^{+}	Cl^{-}	HCO_3^-	SO_4^{2-}	SiO_2	TDS
Group 1	249.28	7.52	19.24	3.36	11.58	11.08	4	141.02	4	22.15	216.50
Group 2	314.3	6.34	24.08	9.04	15.44	1.45	2	205.57	3	7.18	268.00
Group 3	401.45	7.00	37.23	6.82	9.88	27.60	11	199.47	8	8.10	308.00
Group 4	90.00	7.81	0.67	0.19	0.32	9.92	2	67.71	2	2.03	85.00

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