

Hydrogeochemical Characterization and Water Quality Assessment in Manjo, Cameroon

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Abstract: The seasonal variability of hydrogeochemistry and water quality in the Manjo area was investigated to ascertain its suitability for domestic and agricultural purposes. Thirty-five (35) water samples (20 in the dry and 15in the wet seasons) were collected and analyzed for major ions. Physio-chemical parameters (pH, electrical conductivity, total dissolved solids) were measured in situ. Results revealed acidic to basic waters with low mineralization in the two seasons. During the dry season, sodium (Na⁺) dominated the cation composition, while calcium (Ca²⁺) became dominant in the wet season. Bicarbonate $(HCO₃-)$ remained the primary anion in both seasons. Incongruent dissolution of silicate minerals, cation exchange, and little contribution from anthropogenic activities were identified as the main controls of water chemistry. The major ions met the World Health Organization (WHO) drinking water guidelines but nitrate $(NO₃-)$ in some samples exceeded the limit. Most water samples were classified as slightly hard. The water sources were suitable for agricultural purposes based on various parameters (EC, SAR, KR, RSC). The baseline hydrochemical data realized will be useful for the sustainable management and development of water resources.

Keywords: Hydrogeochemistry, water quality, Manjo, Cameroon.

Article Highlights

- 1. A study in Manjo, Cameroon found good quality water sources for drinking and agriculture.
- 2. Nitrate contamination exceeding WHO limits in some groundwater sources raises concerns.
- 3. Sustainable water management practices are recommended to safeguard Manjo's water future.

INTRODUCTION

Limited hydrogeochemical data hinders sustainable groundwater management in Africa**,** where over 80% of the population relies on this resource for drinking (Adelana et al., 2011). Lack of access to good water and the understanding of water chemistry are crucial for assessing drinking water quality and agricultural suitability (Gupta et al., 2009). The availability of fresh water is necessary for any meaningful socio-economic development (Wotany et al., 2021). Geochemical studies reveal the influence of geology and land use on water quality (Edmunds and Smedley, 1996). Groundwater contamination is a growing concern due to population growth, agricultural expansion, and inadequate waste management, further exacerbated by climate change (Laferriere et al., 1996; Conway et al., 2009). Despite significant groundwater resources in Cameroon (Taupin et al., 2000), uneven distribution and lack of comprehensive data hinder effective management (GWP-

CAFTAC2010; Wirmvem et al., 2014a). Silicate weathering and cationic exchange are key geogenic processes influencing water chemistry (Ako et al., 2012; Fantong et al., 2010; Wotany et al., 2013; Akoachere et al., 2019., Menti et al.,2023). Anthropogenic activities play a role in some areas (Njitchoua and Ngounou-Ngatcha, 1997; Fantong et al., 2009, Eneke et al., 2011; Wotany et al., 2019). Access to potable water is a challenge in the area of study where residents rely on unprotected groundwater and surface water sources for domestic purposes. Due to limited hydrochemical data, the study aimed to assess the physio-chemical characteristics and groundwater quality for sustainable water management and development in the study area.

Location of Study Area

The study area encompasses 305 km² along the Douala-Nkongsamba road in Cameroon's Littoral Region (Figure 1). This region, bordering Nlonako and Loum districts to the north and south respectively, features diverse topography ranging from 450m to 1200m in elevation. Prominent landmarks include Mount Koupe and Mount Nlonako, while the Dibombe River and its tributaries are the area's major water bodies.

Figure 1: Location Map (georeferenced) of Manjo and environs

Geological Setting of the Study Area

Located within the Cameroon Volcanic Line (Tchouankoue et al., 2012), dominated by igneous and metamorphic rocks (Figure 2), notably, the Tombel graben features, volcanic cones, basaltic lava flows, and plutonic complexes (Njome et al., 2005). Fracture lines in these formations act as infiltration zones, forming aquifers with good porosity and permeability.

Figure 2: Geologic map of the study area

Climate

The tropical climate features a pronounced wet season (April - October) and a dry season (November - March). Manjo experiences an average temperature of 24.3°C and annual rainfall of 2924 mm, with the highest rainfall in September (497 mm) and the lowest in December (23 mm).

Drainage and Topography

The area exhibits dendritic drainage patterns (Figure 3) with fast-flowing streams and tributaries, especially in steeper areas. The Dibombe River, flowing north to south, serves as the primary drainage channel, receiving numerous tributaries. The region's elevation ranges from 450 meters (South) to 1200 meters (North) (Figure 3). Manjo is surrounded by mountain ranges, with prominent peaks like Manengouba (2400m), Koupé (2070m), and Nlonako (1800m).

Figure 3: Drainage and topography map (georeferenced) of Manjo.

Materials and Methods

Sample collection and preservation

Field Measurements:

Water sampling was done in January in the dry season and June in the wet season from pump wells, open wells, springs, and streams. Samples were filled in pre-rinsed polyethene bottles and filtered using a 0.20 μ m filter. Samples for major ion analysis and bicarbonate (HCO₃⁻) alkalinity were separated and stored appropriately. Samples were kept cool (4°C) during transport.

Physical parameters (pH, electrical conductivity (EC), total dissolved solids (TDS), and temperature) were measured in situ using a calibrated handheld meter. GPS coordinates were recorded for each sampling location. Bicarbonate analysis was performed within 8 hours of sampling using acid titration.

Chemical Analysis:

Major ions and dissolved silica $(SiO₂)$ were analyzed at Tokai University Japan.

Cations: Microwave plasma atomic emission spectroscopy (MP-AES) was used for analysis.

Anions: Ion chromatography (IC) was employed with suppressed conductivity detection.

Data Quality Assurance:

The charge balance principle was used to ensure the reliability of chemical measurements. Measured ion concentrations were converted to milli-equivalent units and compared to verify electrical neutrality (balance of positive and negative charges).

(4)

 $CB = \frac{\sum \text{cations (meq/L)} - \sum \text{anions (meq/L)}}{\sum \text{cations (meq/L)} \sum \text{enions (meq/L)}}$ ∑ cations (meq⁄L)+ ∑ anions (meq⁄L)

(1)

where: $CB = \text{charge balance in percentage}$

The charge balance principle (Domenico & Schwartz, 1990) assesses the reliability of chemical analyses. Measured cation and anion concentrations are converted to milliequivalent units and compared. An acceptable balance reflects electrical neutrality (charge balance error $\leq \pm 5\%$).

Data analysis:

Hydrochemical Facies.

A Piper diagram (using RockWorks15) was used to visually represent water chemistry based on major ions, and identify water types and potential mixing zones.

A stiff diagram (generated by RockWorks15) was used to illustrate the ionic composition of water samples, aiding in visualizing spatial changes.

Mineral Saturation:

The Saturation Index (SI) was calculated to indicate a mineral's stability in water (Freeze & Cherry, 1979) where:

SI < 0: Undersaturated - mineral may dissolve.

 $SI = 0$: Saturated - the mineral is in equilibrium with water.

 $SI > 0$: Supersaturated - mineral may precipitate.

Correlations and Hydrochemical Processes:

The Pearson correlation matrix helped identify relationships between water chemistry variables, potentially revealing the origin of ions and dominant processes (Helena et al., 2000).

Gibbs Diagrams:

Gibbs ratios $[(Na^+ + K^+) / (Na^+ + K^+ + Ca^{2+})$ and Cl⁻ / (Cl⁻ + HCO₃⁻)] plotted against Total Dissolved Solids (TDS) were used to identify the dominant environmental controls on water chemistry (Gibbs, 1970). The resulting diagram indicates the influence of precipitation, water-rock interaction, or evaporation.

Chloro-Alkaline Indices (CAI)

CAI1 and CAI2 indicated the type of ion exchange between groundwater and its surrounding rock. Positive values indicate a direct exchange (Na⁺ & K⁺ for Mg²⁺ & Ca²⁺), while negative values indicate an indirect exchange (Ca²⁺ & Mg²⁺ for Na⁺ & K⁺)

Chloro-alkaline Indices

$$
CAI 1 = CI - (Na+ + K+)/CI
$$
\n
$$
CAI 2 = CI - (Na+ + K+)/SO42- + HCO3- + CO32+ + NO3-)
$$
\n(4)

Water-Rock Interaction:

The weathering index (RE) by Tardy (1971) was employed to assess water-rock interaction, focusing on the ratio of Si (relatively immobile) to Al (mobile) remaining after weathering removes K, Ca, and Na.

Silicate Weathering:

Ionic ratios (Na/Cl, Na/Ca, HCO_3 ⁻/SiO₂, HCO_3 ⁻/ Σ anions) were calculated to further investigate the influence of silicate weathering on water chemistry.

Water Quality Parameters for agricultural purposes was employed:

1.
$$
Na\% = \frac{Na^+ + K}{Na^+ + Ca^2 + + Mg^2 + + K^+} \times 100
$$
 (6)

2.
$$
RSC = (CO_2^- + HCO_3^-) - (Mg^{2+})
$$
 (7)

3.
$$
SAR = \frac{Na^{+}}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}}
$$
 (8)

4. Kelly ratio =
$$
\frac{Na^+}{Ca^{2+} + Mg^{2+}}
$$
 (9)

RESULTS AND DISCUSSION

Physico-chemical characteristics of water samples

The study revealed slight variations in water quality parameters between the seasons (Tables 1a and b). The pH was acidic to basic, ranging from 5.1 to 7.6 (mean = 6.45) in the dry season and 5.5 to 7.5 (mean = 6.51) in the rainy season. Acidic to basic pH (5.1-7.6) reflects mineral processes, biochemical activity, and dissolved CO2 (Freeze & Cherry, 1979; Wotany et al., 2014). The Electrical Conductivity varied between 13 and 232 μ S/cm in the dry season and 12 to 253 μ S/cm in the rainy season. A measure of total dissolved solid ranged from 7 to 116 mg/l in the dry season and 6 to 132 mg/l in the rainy season. Low electrical conductivity (EC) and total dissolved solids (TDS) indicate generally fresh water with low mineralization (Ako et al., 2011; Ngai 2023).

NB: All the variables (cations, anions, and Total Dissolved Solids) are in mg/l. EC Electrical Conductivity is in $\mu s/cm$; SD Standard deviation, OW = Open wells, PW = Pump wells, $SP =$ Springs, $ST =$ Stream, and $WF =$ Waterfall.

Table 1b: Physio-chemical results of groundwater and surface water in Manjo and environments during the rainy season

Conductivity is in $\mu s/cm$; SD= Standard deviation, OW = Open wells, PW = Pump wells, $SP =$ Springs, $ST =$ Stream

The low major ion concentrations in groundwater (Table 1a and b) depict low rock water interactions and short residence time (Edmunds Smedley, 1996; Edet, 2009; Wirmvem *et al.,* 2013b). The dominance of Na, Ca, and Mg in the water could be attributed to dominant silicate weathering, with little contribution from carbonate weathering (Abu-Rukah and Ghrefat, 2004).

Hydrochemical facies

The Piper diagram revealed three dominant water types (Figure 4).

Dry Season:

CaHCO₃ (Calcium-bicarbonate): 13 samples (65%)

NaCaHCO³ (Sodium-Calcium bicarbonate): 6 samples (30%)

NaCl (sodium chloride): 1 sample (5%)

Rainy Season:

CaHCO³ (Calcium-bicarbonate): 60% of samples

NaCaHCO₃ (Sodium-calcium bicarbonate): 35% of samples

NaCl (Sodium chloride): 5% of samples

Figure 4: Piper diagram showing the main hydrochemical facies of groundwater during the (a) dry season and (b) rainy seasons (Piper 1994).

There is a shift towards a higher proportion of CaHCO₃ water type during the rainy season. The presence of CaHCO₃ signifies shallow fresh water and NaHCO₃ water signifies deep fresh groundwater from mineral dissolution (silicate minerals) during recharge of freshwater (Ako *et al.,* 2011; Wotany *et al.,* 2014).

The stiff diagram (Figure 5) provides further insight into water types for specific sampled sources:

Springs (SPO1-8): NaHCO₃ water type, indicated by a slightly higher horizontal extension of Na⁺ $+ K^{+}$ compared to other cations and a dominant extension of HCO₃.

Open Wells (OW1, 2, 4, 5, 6): Primarily NaHCO₃ water type (95%) with a similar pattern to springs (higher $Na^+ + K^+$ and HCO_3^- extension). Open well OW3 exhibits a distinct NaCl water type signature with a significantly higher extension of $Na^+ + K^+$ and Cl⁻ compared to other ions.

Pump well (PW01): MgHCO₃ water type, evident from a higher extension of Mg^{2+} and HCO₃-.

Streams (ST14) and Waterfall (WF01): CaHCO₃ water type, characterized by a dominant extension of HCO_3^- and Ca^{2+} as in Lumnwi et al.,2023.

Figure 5: Stiff diagram of concentrations of water samples.

Geological controls of groundwater chemistry

Saturation indices (SI) for anhydrite ranged between -6.92 to -4.51 (Table 2) accounting for 100% of the total samples being undersaturated. SI for aragonite ranged between -5.53 to -0.99 with all the samples being undersaturated. SI for chrysolite, dolomite, gypsum, halite, sylvite, sepiolite, and amorphous silica were undersaturated for all the water samples. SI for chalcedony ranged between - 0.48 to 0.43 with just 35% of the samples being undersaturated. Eighty-five per cent (85%) of the samples were supersaturated with quartz (SI ranged between -0.05 to 0.86). This dominance could be attributed to the weathering of granitic rocks since it is one of the dominant rock types in the study area. The SI for talc ranged between -20.46 to 0.61 with just one sample slightly supersaturated (5%). The undersaturation of the Sulphate mineral (Gypsum) suggests the absence of this mineral in the host rock. The concentration of dissolved silica ranged between 5.77 to 44.70mg/l with 80% of the water samples having a concentration higher than the solubility of quartz (6.0mg/l). This can be attributed to the dissolution of quartz and a lesser degree chalcedony. Similar results had been reported by Ako *et al.* (2012) in the Mount Cameroon area.

Table 2: Summary statistics of the major mineral phases in the water sources during the dry season.

Mineral stability is an important approach in which equilibrium between clay minerals and natural water can be verified through thermodynamic data. The plot of K^+ and Na^+ silicate systems (Figure 6) after Garrels and Christ (1965) shows that water in the study area is in the range of the stability field of kaolinite with little contribution from Na-Montmorillonite (5%), which implies that the chemistry of the water favours kaolinite formation. The formation of kaolinite rather than gibbsite represents less rapid flushing, where less silica is removed during weathering (Abu-Rukah and Ghrefat, 2004). The incongruent dissolution of silicate minerals (anorthite, albite, K-feldspars, pyroxene, and clinopyroxene), which produces kaolinite plus cations, can be written separately as follows (Mazor,2004):

Anorthite: CaAl₂SiO₂O₈ + 2CO₂ + 3H₂O \rightarrow Al₂SiO₅(OH)₄ + Ca²⁺ + 2HCO₃

Albite: $2NaAlSiO₂O₃ + 2HCO₃ + 9H₂O \rightarrow Al₂SiO₅(OH)₄ + 4H₄SiO₄ + 2Na⁺ + 2HCO₃$

K - feldspar: $2KAISi₃O₈ + 6H₂O + CO₂ \rightarrow Al₂SiO₅(OH)₄ + 4SiO (OH)₂ + K₂CO₃$

Pyroxene: $(Ca, Fe, Mg)(SiO₃) + 2H₂O + 2CO₂ \rightarrow (Ca, Fe, Mg)(HCO₃)₂ + SiO(OH)₂$

Clinopyroxene: $(CaMg_{0.7}Al_{0.6}Si_{1.7})O_6 + 4CO_2 + 4H_2O \rightarrow 0.3Al_2SiO_5(OH)_4 + Ca^{2+} + 0.7Mg^{2+} +$ $1.1H_4SiO_4 + 3.4HCO_3$

Figure 6: Mineral stability diagrams in the system K₂O-Na₂O-Al₂O₃-SiO₂-H₂O of waters in the study area (Abu-Rukaet al., 2004).

In other to further confirm the clay minerals obtained from the $K_2O-Na_2O-Al_2O_3-SiO_2-H_2O$ system, the characterization of water–rock interaction was done by deducing the weathering index (RE).

A scale of RE variations corresponding to the type of weathering shows that: if RE is ≤ 0 , the weathering process is allitisation (an advanced stage of weathering in which Al and Fe accumulate at the expense of other ions such as alkalis, alkaline earth, and silica, which is removed from soils in aqueous phase) and gibbsite is the main mineral formed; if 0 to \leq 2, the weathering process is monosiallitisation, which results in kaolinite formation; if RE is ≥ 2 , the weathering process is bisiallitisation where kaolinite and montmorillonite are the main minerals formed. All the samples had $RE > 2$, hence confirming the mineral phases obtained from the mineral stability diagrams using the thermodynamic approach. This RE range suggests that bisiallitization is the main weathering process taking place in the study area. Under this weathering process, weak to moderate leaching favors an approximate balance between $SiO₂$ and cations which yields the formation of 2:1 clays (Tardy, 1971). Kaolinite was the major clay mineral in both ground and surface water in the Mount Cameroon area (Ako *et al.,*2012).

Meybeck (1987) used the Na/Cl molar ratio to study silicate weathering reactions and concluded that Na/Cl>1 reflects $Na⁺$ release from silicate weathering whereas $Na⁺/Cl⁻$ molar ratio approximately equal to 1 is usually attributed to halite dissolution (Cendon *et al.,* 2010). The Na⁺/Cl⁻ molar ratio for the dry season in ground and surface water had a computed mean of 5.75 and 10.12 respectively while that for the rainy season had a mean of 6.84 and 4.0 for ground and surface water respectively (Table 3a and 3b). The mean concentration for both seasons is greater than 1 with about 95% of the samples having molar concentration higher than 1. This proves that the hydrochemical process that controls the groundwater chemistry is silicate weathering.

	GROUNDWATER $(n=15)$				SURFACE WATER $(n=5)$			
Parameters	Minimum	Maximum	Mean	STD	Minimum	Maximum	Mean	SD
$Na^+/Cl^-(mol/l)$	0.89	17.78	5.75	4.20	5.53	13	10.12	3.44
Na^{+}/Ca^{2+} (meq/l)	0.84	2.43	1.26	0.41	0.52	1.08	0.91	0.23
$HCO3/SiO2 (mol/l)$	0.48	1.93	1.10	0.37	0.91	1.35	1.06	0.17
$HCO3/\sum$ anions (meq/l	0.3	0.97	0.801	0.20	0.91	0.97	0.94	0.02
RE (mol/l)	2.10	5.04	3.72	0.66	2.91	3.55	3.16	0.26
$CAI1$ (meg/l)	-20.16	-0.89	-6.98	4.74	-15.22	-7.02	-11.95	3.85
$CAI2$ (meq/l)	-0.78	-0.34	-0.52	0.11	-0.53	-0.34	-0.47	0.08
Total Hardness as CaCO ₃ (mg/l)	3.25	82.16	21.03	18.90	10.69	52.09	22.83	17.20
SAR(meq/l)	0.27	0.80	0.58	0.15	0.34	0.47	0.38	0.05
Kelly ratio(meq/l)	0.40	1.17	0.73	0.21	0.26	0.54	0.45	0.11
RSC (meq/l)	-0.35	0.13	0.00	0.13	-0.25	0.04	-0.04	0.12

Table 3a: A statistical summary of ratios between some ionic species in the analysed water during the dry season.

Table 3b: A statistical summary of ratios between some ionic species in the analysed water during the rainy season**.**

	GROUNDWATER $(n=13)$				SURFACE WATER $(n=2)$			
Parameters	Min	Max	Mean	STD	Min	Max	Mean	STD
$Na^{\dagger}/Cl^{\dagger}$	0.28	34.74	6.84	9.08	0.92	7.09	4.00	4.36
Na^{\dagger}/Ca^{2+}	0.42	1.70	0.99	0.35	0.47	1.12	0.79	0.46
$HCO3/\sum$ anions	0.14	6.34	2.60	1.86	2.80	7.63	5.21	3.42
CAI1	-38.76	-0.30	-8.21	10.02	-0.85	-7.79	-4.32	4.91
CAI ₂	-0.64	-0.11	-0.43	0.17	-0.08	-0.45	-0.26	0.26
Total Hardness as CaCO ₃ (mg/l)	2.53	126.33	25.11	31.83	7.47	52.8	30.13	32.06
SAR	0.11	0.93	0.52	0.32	0.31	0.31	0.31	0.00
Kelly ratio	0.26	1.09	0.57	0.27	0.21	0.56	0.39	0.25
RSC	-1.08	0.16	-0.08	0.33	-0.27	0.041	-0.11	0.22

The mean $HCO₃/\Sigma$ anions ratio in the water for both seasons is > 0.8 (Table 3a and 3b) samples confirming silicate weathering.

To further determine the likely influence of silicate dissolution, the molar ratio of $HCO₃/SiO₂$, relationship was examined. If the $HCO₃/SiO₂$ ratio is greater than 10, (that is, $HCO₃>SiO₂$), carbonate weathering predominates. However, if the ratio is low and especially \leq , silicate weathering predominates (Hounslow, 1995). The ratio for ground and surface water was 1.10 and 1.06 respectively (Table 3a). Since the ratios of all the individual samples in the study area were <5, silicate weathering is hence the active process occurring in the study area. Similar observations of silicate dissolution in granitic formations (Njitchoua and Ngounou-Ngatcha, 1997; Fantong *et al.,* 2009) and volcanic terrains (Tanyileke *et al.,* 1996; Ako *et al.,* 2012) along the CVL have been reported.

Also, $Ca^{2+} + Mg^{2+}$ versus $SO_4^{2-} + HCO_3$ relationships were examined. Figures 7a and 7b depict a deficiency of $Ca^{2+} + Mg^{2+}$ relative to $SO_4^{2-} + HCO_3$. This deficiency suggests the likely influence of silicate dissolution (Wirmvem *et al.,* 2013).

Figure 7: Plot showing deficiency in $Ca^{2+} + Mg^{2+}$ about $SO_4^{2-} + HCO_3^-$ in water sources during the dry and rainy season.

Gibbs plot in (Figures 8a and 8b) shows that the majority of the water samples plot in the water interaction zone which further confirms incongruent weathering of silicate minerals as the dominant process (Njitchoua and Nganou-Ngatcha, 1997; Fantong *et al.,* 2009; Wirmvem *et al.,* 2012; Wotany et al., 2013).

Figure 8. Mechanisms controlling the chemistry of the water sources (after Gibbs, 1970) (a) dry season (b) rainy season**.**

The nature of ion exchange was determined by calculating Chloro-Alkaline Indices (CAI) (Schoeller, 1965). All samples showed negative values for CAI 1 and CAI 2 for both seasons (Figures 8a and 8b). This indicates that Mg^2 and Ca^{2+} in groundwater were being exchanged with $Na⁺$ and $K⁺$ in rocks; hence, favouring cation exchange reactions (chloro-alkaline disequilibrium) (Gupta et al., 2009). In a situation where a positive CAI1 and CAI2 exist, it indicates reverse-ion exchange between Na⁺ and K⁺ in groundwater with Ca²⁺ or Mg²⁺ in rocks (Jankowski et al., 1998). Since the exists incongruent weathering of silicate minerals to clay minerals, cation exchange is likely to occur since clay mineral surfaces are suitable cation-exchange sites. Thus, through cation exchange, Na⁺ and K⁺ can easily substitute for Ca²⁺ and Mg²⁺on cation adsorption sites in the aquifer mass, which could give rise to the mixed (CaNaHCO₃) water type (Ako *et al.*, 2011).

The negative values of Chloro-Alkaline Indices (CAI1 and CAI2) for groundwater sources (Table 3a and 3b) in the two seasons indicate an indirect cation exchange process (Appelo & Postma, 2005). This suggests an exchange of Ca^{2+} and Mg^{2+} from rock minerals with Na⁺ and K⁺ in the groundwater.

Negative Chloro-Alkaline Indices (Figures 9a and 9b) indicate an exchange of Mg^{2+} and Ca^{2+} for Na⁺ and K⁺ due to the presence of clay minerals (Schoeller, 1967; Ako et al., 2011).

Figure 9: Chloro Alkali Index 9(a) and 9(b) in groundwater for both seasons in the study area showing negative indices.

The major ion chemistry of groundwater and compositional relations among ionic species can reveal the origin of solutes and processes that generated an observed water composition (Hounslow, 1995; Demlie *et al.,* 2007; Cendon *et al.,* 2011; Wirmvem *et al.,* 2013b).

The statistical analysis revealed strong positive correlations (r² values close to 1) between several water chemistry parameters during both dry and rainy seasons (Tables 4 and 5). These correlations suggest that the concentrations of these ions are likely influenced by similar factors.

Electrical Conductivity (EC) and Total Dissolved Solids (TDS): A high correlation indicates that TDS is a major contributor to electrical conductivity, which reflects the total dissolved ions in water. **EC/TDS with Major Cations (Na, Ca):** Positive correlations suggest that these cations significantly contribute to the overall ionic content and conductivity.

Cations (Na, Ca) and Anion (HCO3): Positive correlation implies that these ions might originate from the same weathering processes or dissolution of similar rock minerals.

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Table 5. Correlation coefficient matrix of all the analyzed water (n =15) for rainy season samples.

Bold values indicate correlations between physicochemical parameters. The double asterisk (**) indicates a very strong positive correlation between the parameters.

Human Impact on Groundwater Quality: Nitrate Contamination

Natural processes like biological fixation and precipitation contribute some nitrate (Berner & Berner, 1987). However, human activities significantly increase nitrate levels: Industrial sewage and refuse dumps (Ako et al., 2012), Agricultural fertilizers, and pesticides (since the 1970s) (Majumdar & Gupta, 2000). High nitrate concentrations were observed in some wells, particularly near pit latrines and agricultural areas (Manengole well - 36.2 mg/l). This suggests nitrate contamination from; improper sanitation practices (pit latrines) and agricultural practices (use of fertilizers and pesticides).

Naturally, nitrate levels are minimal in the area's crystalline rocks (Ako et al., 2012). The positive correlation between nitrate (NO₃) and chloride (Cl) in both seasons ($r^2 > 0.8$) further indicates human influence on groundwater quality. Health Risks of high Nitrate include methemoglobinemia (blood disorder), gastric cancer, goiter, birth malformations, and hypertension (Majumdar & Gupta, 2000). Figure 10 shows nitrate $(NO₃-)$ concentrations plotted against well depth. Key observations are:

Significantly higher nitrate is observed in the first 12 meters, decreasing with depth. This suggests contamination from surface activities (likely human sources), Open wells show a slight nitrate increase during the rainy season, potentially due to increased contaminant mobilization. The nitrate distribution highlights the unconfined nature of the aquifer, making shallow groundwater sources

(open wells and springs) more susceptible to contamination.

Figure 10: Plot of depth of wells and boreholes versus nitrate concentrations of groundwater

Suitability for Drinking and Domestic Use

Assessing the suitability of groundwater for drinking and domestic purposes is crucial, as safe drinking water is fundamental to human health and development (WHO, 2003, 2004).

The analytical results have been evaluated to determine the suitability of groundwater for drinking and domestic use according to the standards set by the World Health Organization (WHO, 2011) (Tables 6 and 7).

Table 6: Groundwater quality in compliance with WHO (2011) drinking water standards during the dry season*.*

Parameters		Ground Water $(N=15)$		WHO	% sample above (or out of)
	Min	Max	Mean	(2011) limit	WHO guideline
pН	5.1	7.3	6.16	$6.5 - 8.5$	50
EC	13	232	80.47	750	0
$Na^+(mg/l)$	1.55	15.20	6.06	200	θ
K^+ (mg/l)	0.23	8.30	2.99	100	0
$Ca^{2+} (mg/l)$	0.55	15.65	4.85	75	0
$Mg^{2+} (mg/l)$	0.43	10.50	2.17	30	0
Ba^{2+} (mg/l)	0.00	0.20	0.04	2	θ
$Cl^{(mg/l)}$	0.29	16.40	2.79	250	θ
$NO3$ (mg/l)	0.22	36.20	8.92	10	19
SO_4^2 (mg/l)	0.05	1.54	0.65	250	θ
$HCO3$ (mg/l)	6.71	85.80	25.59	200	0
TDS (mg/l)	7.00	116	40.20	500	0
TH $(mg/ICaCO3)$	3.25	82.18	21.03	100	Ω

Groundwater quality in compliance with WHO

Table 7: Groundwater quality in compliance with WHO (2011) drinking water standards during the rainy season*.*

SO_4^2 (mg/l)	0.05	4.28	0.78	250	
$HCO3$ (mg/l)	3.10	89.8	26.35	200	
TDS	6.00	132	51.00	500	
Total hardness (TH)	252 ر ر.ر	26.33	25.78	00	

Table 8: Surface water quality in compliance with WHO (2011) drinking water standards during the dry season.

During the dry season, approximately 20% of the pH readings for surface waters exceeded the WHO guideline (Table 8). However, during the rainy season, all the pH readings for surface water remained within the limits (Table 9). The physicochemical parameters and major ion concentrations recorded for both seasons were within the WHO limits.

Table 9: Surface water quality in compliance with WHO (2011) drinking water standards during the dry season.

	Surface Water $(N=2)$			WHO	% sample above (or out
Parameters	Min	Max	Mean	(2011) limit	of) WHO guideline
pH	7.20	7.50	7.35	$6.5 - 8.5$	
EC	26.00	143.00	84.5	750	θ
$Na^+(mg/l)$	1.96	5.24	3.6	200	θ
K^+ (mg/l)	0.34	1.70	1.02	100	θ
$Ca^{2+} (mg/l)$	1.52	9.80	5.66	75	θ
$\overline{\text{Mg}^{2+}}$ (mg/l)	0.89	6.90	3.90	30	θ
$Cl^-(mg/l)$	0.43	8.77	4.60	250	θ
$NO3^-(mg/l)$	0.58	1.90	1.24	10	θ
$SO_4^{2-} (mg/l)$	0.18	0.37	0.28	250	θ
HCO ₃ (mg/l)	11.70	48.70	30.20	200	θ
TDS (mg/l)	13.00	71.00	42	500	θ
TH (mg/lCaCO ₃)				100	0

Hardness

Calcium and magnesium hinder soap lathering, raise water's boiling point, and potentially lead to pipe encrustation. The majority of groundwater is slightly hard (Tables 10 and 11). While hard water is safe for consumption, it can cause inconveniences in domestic chores.

Table10: Groundwater classification based on total hardness (TH) after Driscoll (2009) for dry season samples (n=15)

Total hardness (TH) as CaCO ₃ (mg/l)	Water type	Number of groundwater samples	Percentage of groundwater samples
	Soft		
$9 - 60$	Slightly hard		
60-120	Moderately hard		

Agricultural suitability

Salinity buildup from irrigation water can harm crops and soil. Electrical conductivity (EC) and Sodium Absorption Ratio (SAR) are key indicators of irrigation water suitability (Richards, 1954). **Sodium Adsorption Ratio (SAR):** The relatively low SAR values (Tables 3a and 3b) (mean dry season for groundwater: 0.58, mean rainy season groundwater: 0.52) indicate the suitability of the water sources for irrigation on most soils according to the United States Salinity Laboratory classification (Richards, 1954).

Kelly Ratio: Similar to SAR, the Kelly ratio values (mean dry season for groundwater: 0.73, (Tables 3a and b) mean rainy season for groundwater: 0.57) also indicate a low risk of sodium problems in irrigated soils.

All water samples had EC below 250 μ S/cm, indicating excellent suitability of water samples for irrigation (Tables 12 & 13).

Table 12: Suitability of groundwater and surface water for agricultural purposes during the dry

season.

Quality parameter	Range of values	Description	Number of groundwater samples	Number of surface water samples	$%$ of groundwater sample	% of surface water sample
	< 250	Excellent	12	2	92	100
EC (μ s/cm)	250-750	Good			8	
(Raghunath,	750-2,000	Permissible		$\overline{}$		
1987)	2000-3000	Doubtful				
	>3,000	Unsuitable				
SAR (Richards,	<10	Excellent	13	$\overline{2}$	100	100
	$10 - 18$	Good				
	18-26	Doubtful				
1954)	>26	Unsuitable				
	$<$ 20	Excellent		$\overline{}$		
Na $%$	20-40	Good	6	2	46	100
(Raghunath,	$40 - 60$	Permissible	7		54	
1987)	60-80	Doubtful				
	>80	Unsuitable	$\overline{}$	$\overline{}$		
RSC	< 1.25	Excellent	13	2	100	100
(Yidana et	1.25-2.5	Acceptable				
al., 2010)	>2.5	Unacceptable				

Table 13: Suitability of groundwater and surface water for agricultural purposes during the rainy season.

Both USSL (1954) and Wilcox (1955) classifications placed all water samples in zones favourable for irrigation due to low salinity and sodium content. (Figures 11 and 12). This is positive for the inhabitants that rely heavily on the water sources for irrigation.

Figure 11: United States Salinity Laboratory (USSL) classification of water samples during (a) dry season and (b) rainy season

Figure 12: Wilcox (1955) diagram showing irrigational suitability in the study area during (a) the dry season and (b) the rainy season.

Conclusion

The hydrogeochemical investigation revealed key findings regarding water quality and suitability. The water sources were generally fresh (low mineral content, pH 5.1 -7.6) with dominance of Na⁺, $Ca²⁺, Mg²⁺, and HCO₃⁻ ions. Silicate weathering and cation exchange were the primary controls of$ water chemistry. Clay mineral formation (kaolinite, montmorillonite) was also identified.

Nitrate contamination indicated human influence. Most water samples met the WHO drinking water guidelines for major ions. A high nitrate level in some samples is a call for concern and regular monitoring. The water sources were suitable for agricultural purposes. To ensure sustainable water resource management, the study recommends maintaining proper sanitation practices; regulate the use of fertilizers to minimize nitrate contamination.

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REFERENCES

- 1. Abu-Ruka, Y. and Ghrefat, H.A. (2004). Ion chemistry of waters impounded by the Ziqlab dam, Jordan, and weathering processes – a case study. *Int. J. Environment and Pollution*, Vol. 21, No. 3, pp.263–276.
- 2. Ako, A. A., Shimada, J., Hosono, T., Ichiyanagi, K., Nkeng, G. E., Fantong, W. Y., Eyong, G. E. T., Roger, N. N. (2011). Evaluation of groundwater quality and its suitability for drinking, domestic, and agricultural uses in the Banana Plain (Mbanga, Njombe, Penja) of the Cameroon Volcanic Line*. Environ. Geochem. Health* 33:559-575.
- 3. Ako, A. A., Shimada, J., Hosono, T., Kagabu, M., Akoachere, R. A., Nkeng, G. E., Eneke, G.T., Fouepe, A.T. (2012). Spring water quality and usability in the Mount Cameroon area revealed by hydrogeochemistry. *Environ. Geochem. Health* 34 (5): 615-39.
- 4. Akoachere, R.A., Sonia, E.E., Thomson, A.E., Sophie, N.E., Simon, N.L., Diana, B. T., Nji, B.N. (2019). Seasonal Variations in Groundwater of the Phreatic Aquiferous Formations in Douala City-Cameroon: Hydrogeochemistry and Water Quality. *Open Access Library Journal*, Volume 6, e5328.
- 5. Appelo, C. A. J. and Postma, D. (2005). *Geochemistry, groundwater, and pollution* (2nd ed.). Amsterdam: Balkema, p 635.
- 6. Berner, E. K., & Berner, R. A. (1987). *The global water cycle: Geochemistry and environment*. Englewood Cliffs: Prentice Hall.
- 7. Cendon, D. I., Larsen, J. R., Jones, B. G., Nanson, G. C., Rickleman, D., Hankin, S. I., Pueyo, J. J., Maroulis, J. (2010). Freshwater recharges into a shallow saline groundwater system, Cooper Creek floodplain, Queensland, Australia. *J. Hydrol*. 392 (2-4): 150-163.
- 8. Conway, G. (2009). The Science of Climate Change in Africa. *Impacts and adaptation. Discussion paper* no 1, Imperial College, London, pp:24.
- 9. Demlie, M., Wohnlich, S., Wisotzky, F., and Gizaw, B. (2007). Groundwater recharge, flow, and hydrogeochemical evolution in a complex volcanic aquifer system, central Ethiopia. *Journal of Hydrogeology*. 15, 1169–1181.
- 10. Domenico, P. A., Schwartz, F. W. (1990). *Physical and chemical Hydrogeology*. New York: John Wiley and Sons. 411:485-497.
- 11. Driscoll (2009). Water hardness is based on the concentration of calcium and magnesium. In: Poells, D.J., Smith, G.J. (Eds.). *Encyclopedic Dictionary of Hydrogeology*. Burlington, MA, USA: Academic Press.
- 12. Edet, A. E. (2009). Characterization of groundwater contamination using factor analysis in the Niger Delta (Nigeria). *J. Hydrol. Eng*. 14(11):1255-1261.
- 13. Edmunds, W. M., Smedley, P. L. (1996). Groundwater geochemistry and health: An overview. In: Appleton, J.D., Fuge, R, McCall, G.J.H (eds.) Environmental geochemistry and health with

special reference to developing countries. *Geological Society Special Publication* No.113, pp. 91-105.

- 14. Eneke, G. T., Ayonghe, S. N., Chandrasekharam, D., Ntchancho, R., Ako, A.A., Mouncherou, O.F., Thambidurai, P. (2011). Controls on groundwater chemistry in a highly urbanized coastal area. *Int. J. Environ. Res*. 5(2):475-490.
- 15. Fantong, W. Y. (2010). Hydrogeochemical and environmental isotopic study of groundwater in Mayo Tsanaga river basin, northern Cameroon: Implication for public groundwater supply management. Ph.D Thesis, University of Toyama, p. 211.
- 16. Fantong, W.Y., Satake, H., Ayonghe, S.N., Aka, F.T., Asai, K., (2009). Hydrogeochemical controls and usability of groundwater in semi-arid Mayo Tsanaga River Basin, Far North Cameroon. *Environ. Geol*., 58, 1281-1293.
- 17. Freeze, R. A., Cherry, J. A. (1979). *Groundwater*. 2nd ed. Eaglewood Cliff, New Jersey, USA: Prentice Hall, pp. 604.
- 18. Garrels, R.M. and Christ, G.L. (1965) *Solutions, Minerals and Equilibrium*. New York: Harper and Row.
- 19. Gibbs, R. J. (1970). Mechanisms controlling world water chemistry. *Sci*. 17: 1088-1090.
- 20. Gupta, S., Dandele, P.S., Verma, M.B., Maithani, P.B. (2009). Geochemical assessment of groundwater around Macherla-Karempudi area, Guntur District, Andhra Pradesh. *J. Geol. Soc. India* 73: 202-212.
- 21. GWP/CAFTAC (2010). Global Water Partnership Central Africa. Cameroon Report pp.210
- 22. Hounslow, A. W. (1995). *Water quality data: Analysis and interpretation*. Boca Raton: Lewis Publishers.
- 23. Jankowski, J., Acworth, R. I., Shekarforoush, S. (1998). Reverse ion exchange in deeply weathered porphyritic dacite fractured aquifers system, Yass, New South Wales, Austria, In
- 24. Laferriere, J.J., Minvelle, J.L. and Payment, P. (1996). The hog industry and risks to human health. *Bull Inform Health Environ* 7:1-4.
- 25. Lumnwi M., Wotany, E. R., Fantong W. Y., Ayonghe, S. N. (2023). Potable water quality and health nexus in Bafut Sub-Division NorthWest Region – Cameroon. IJISRT, ISSN: 2456-2165
- 26. Majumdar, D., & Gupta, N. (2000). Nitrate pollution of groundwater and associated human health disorders. *Indian Journal of Environmental Health*, 42, 28–39
- 27. Mazor, E. (2004). *Chemical and isotopic groundwater hydrology*. New York: Marcel Drekker Inc.
- 28. Menti, A.N., Wotany, E.R., Christopher, A. et al. Hydrogeochemical characterization of ground and surface water in the eastern part of the Adamawa-Yade domain, BertouaCameroon. Discov Water 3, 10 (2023).<https://doi.org/10.1007/s43832-023-0>
- 29. Meybeck, M. (1987). Global chemical weathering of surficial rocks estimated from river dissolved loads. *Am. J. Sci*. 287:401-428.
- 30. Ngai Nfor Jude, Wotany ER, Agyingi C, Ghomsi FEK, Aurore MKG, Nelson MA, et al. (2023) Hydrogeochemical Characterization of Groundwater Quality, East of Mount Cameroon and West of the Penda Mboko River, Suitability for Drinking and Irrigation Use. J Geol Geophys. 12:10931.
- 31. Njitchoua, R., Ngounou-Ngatcha, B. (1997). Hydrogeochemistry and environmental isotope investigations of the north Diamare Plain northern Cameroon. *J. Afr. Earth Sci*., 25, 307-316.
- 32. Njome, M. S., Suh, C. E. (2005). Tectonic evolution of the Tombel graben basement, southwestern Cameroon. *Episodes*, 28(1), 37–41.
- 33. Piper, A. M. (1944). A graphic procedure in the geochemical interpretation of water analyses. *Am. Geophys. Union Trans.* 25: 914-923.
- 34. Richard, L.A. (1954). *Diagnosis and improvement of saline and alkaline oils*. Washington DC: US Department of Agriculture. p. 60.
- 35. Schoeller, H. (1967). Geochemistry of groundwater. In: Brown, R.H. (Ed.), *Groundwater Studies - An International Guide for Research and Practice*. Paris: UNESCO, pp. 1-18.
- 36. Tanyileke, G.Z., Kusakabe, M., Evans, W.C. (1996). Chemical and isotopic characteristics of fluids along the Cameroon Volcanic Line, Cameroon. *J. Afr. Earth Sci*. 22, 433-441.
- 37. Tardy, Y., (1971). Characterization of the principal weathering types by the geochemistry of waters from some European and African crystalline massifs. *Chem. Geol.***7**, 253-271.
- 38. Taupin, J. D., Coudrain, R. A., Gallaire, R, Zuppi, G. M., Filly, A., (2000). Rainfall characteristics (δ18O, δ2H, $ΔT$, and $ΔHr$) in western Africa: regional scale and influence of irrigated areas. *J Geophys Res* 105: 11911–11924.
- 39. Tchouankoue, J.P., Nicole, A. S. W., Armand, K. D. and Gerhard, W. (2012). Petrology, Geochemistry, and Geodynamic Implications of Basaltic Dyke Swarms from the Southern Continental Part of the Cameroon Volcanic Line, Central Africa. *The Open Geology Journal*, 6, 72-84.
- 40. United States Salinity Laboratory., (1954). *Diagnosis and improvement of saline and alkaline soils*. Washington: US Department of Agriculture.
- 41. WHO (2003). *Nitrate and nitrite in drinking water. Background document for preparation of WHO guidelines for drinking water quality*. Geneva: WHO p.p 1-16.
- 42. WHO (2004). *Guidelines for drinking-water quality* (3rd ed). Geneva: World Health Organization, p. 514. c.
- 43. WHO, (2011). Guidelines for drinking-water quality (4th ed). World Health Organization, Geneva. p. 564.
- 44. Wilcox, L.V. (1955). *Classification and use of irrigation waters*. Washington, D.C.: U.S. Department of Agriculture, Circular 969,
- 45. Wirmvem, M.J., Ohba T, Fantong, W.Y., Ayonghe, S.N., Suila, J.Y., Asaah, A.N.E., Tanyileke, G., Hell, J.V., 2013b. Hydrochemistry of shallow groundwater and surface water in the Ndop plain, North West Cameroon. *Afr. J. Environ. Sci*. *Technol*. 7, 518-530.
- 46. Wirmvem, M.J., Ohba, T., Fantong, W.Y., Ayonghe, S.N., Hogarh J.N., Suila, J.Y., Asaah, A.N.E., Tanyileke, G., Hell, J.V. (2014a). Origin of major ions in monthly rainfall events at the Bamenda Highlands, North West Cameroon. *J. Environ. Sci*. 26, 801-809.
- 47. Wotany ER, Ayonghe SN, Fantong WF, Wirmvem JM, Wantim MN (2014). Hydrochemical characteristics of groundwater in sedimentary, metamorphic and volcanic aquifers in Ndian Division,

South West Region, Cameroon. J Cameroon Acad Sci 11(2 &3):157–170.

- 48. Wotany, E. R., Samuel N. Ayonghe, Mengnjo J. Wirmvem, Wilson Y. Fantong " Physicochemical and Bacteriological quality of water sources in the coast of Ndian, South West region, Cameroon: Health implications" IJTSRD, ISSN: 2456-6470, Volume-3, Issue-5, (2019).pp.1091-1097,<https://doi.org/10.31142/ijtsrd26626>
- 49. Wotany, E. R., Wirmvem, M. J., Fantong, W. Y., Ayonghe, S. N., Wantim, M. N., & Ohba, T. (2021). Isotopic composition of precipitation and groundwater onshore of the Rio del Rey Basin, southwest Cameroon: local meteoric lines and recharge. Applied Water Science, 11(8). https://doi.org/10.1007/s13201-021-01473-7
- 50. Wotany, E.R., Ayonghe, S.N., Fantong, W.Y., Wirmvem, M.J., Ohba, T. (2013). Hydrogeochemical and anthropogenic influence on the quality of water sources in the Rio del Rey Basin, South Western, Cameroon, Gulf of Guinea. *Afr. J. Environ. Sci. Technol*. 7, 1053- 1069.
- 51. Yidana, S.M. (2010). Groundwater classification using multivariate statistical methods: Southern Ghana. *J. Afr. Earth Sci*. 57:455-469.