

Hydrogeochemical and Groundwater Quality Studies in the High Bandama Watershed at Tortiya (Northern of Côte d'Ivoire)

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Abstract

Hydrochemical and groundwater quality of High Bandama watershed were investigated through thirty-five (35) samples composed of boreholes, hand pump wells and traditional wells. The analysis of physico-chemical parameters shows that groundwater is acidic with pH ranges from 3.2 to 6.9 and mean of 5.4. Electrical conductivity (EC) values were generally low and minimum and maximum were respectively 77 $\mu\text{S}/\text{cm}$ and 553 $\mu\text{S}/\text{cm}$ with an average of 250.3 $\mu\text{S}/\text{cm}$. Major cations (Ca^{2+} , Mg^{2+} , Na^{+} and K^{+}) were also generally low. Ca^{2+} and Mg^{2+} are being the most dominants cations with concentration values ranges from 4 - 56 mg/l and 0 - 55 mg/l respectively with mean value of 18.11 and 15.31 mg/l. HCO_3^- is the most dominant anion with minimum and maximum values ranging from 5 to 215 mg/l. According to WHO guidelines, groundwater quality is good for drinking. Piper diagram classified the hydrogeochemical facies into Ca- HCO_3 (48.57%), Ca-Mg- HCO_3 (31.43%), Ca-Mg-Cl (17.14%) and Na-Cl (2.86%) water type with one sample for Na-Cl. Compositional relation with plot of Ca + Mg versus $\text{HCO}_3 + \text{SO}_4$ and Chloro Alkaline Indice (CAI) confirms that the majority of groundwater samples (66.67%) exchange their ions Ca and Mg with Na and K from aquifer materials. Gibbs diagram showed that the rock-water interaction or weathering is the dominant process responsible of water chemistry.

Keywords

Groundwater, Hydrochemical Methods, Waters Types, High Bandama Watershed

1. Introduction

The importance of water and particularly groundwater is not to demonstrate. Accessibility to a safe and reliable source of water is essential for sustainable development. Water may exist in quantity but if its quality is not good, it becomes unsustainable. Groundwater has become the major source of water supply for domestic, industrial and agricultural sectors of many countries (Ghislain et al., 2012). Chemistry of groundwater is an important factor determining its use for domestic, irrigation and industrial purposes. Hydrogeochemical processes that are responsible for altering the chemical composition of groundwater vary with respect to space and time (Sivasubramanian et al., 2013). The hydrogeochemical processes of groundwater system help to obtain an insight into the contributions of rock/soil-water interaction (Senthilkumar & Elango, 2013; Sivasubramanian et al., 2013). Groundwater remains the only drinking water resource in most of the High Bandama Basin rural and urban parts through several boreholes and sometimes hand pump wells or traditional wells. In fact, the high drought occurred in 1983 which led the Ivorian authorities to carry out the project of drinking in many localities. We can cite among these projects the Fund National of Hydraulic (FNH), BADEA, etc. After digging boreholes or wells, water obtained is drunk by population without knowledge of its quality. Few sources of surface water exist in the rural area (rivers, dams, source point). We denoted about 1500 dams but this water is assigned to agriculture use and sometimes fishing. Surface water is subject to variations and their sources deplete in dry period. For these reasons the authorities are focused on groundwater resources even though some boreholes levels decrease in dry season. Since groundwater is not immune to pollution and activities such as mechanized agricultural practices, rapid urbanization as well as domestic and industrial waste can pose a serious threat to groundwater potential in the basin (Gibrilla et al., 2010). The High Bandama Basin is an agricultural area. The use of agricultural inputs such as fertilizers, pesticides represent a threat for groundwater quality. Study hydrogeochemical and groundwater quality of basin become very important. In fact, groundwater quality reflects the impact of change occurs in the area. This study will seek to understand the chemical evolution of the aquifers, groundwater quality and characterize the groundwater system using hydrochemical methods such as compositional relation, cation-exchange and Gibbs diagram.

Study Area

The High Bandama Watershed (HBW) is a sub-basin of Bandama Basin. It is located at the north of Côte d'Ivoire between latitudes 8°40'N and 10°20'N and longitudes 5°W and 6°30'W and covered about a total area of 14,500 km² (Figure 1). The outlet station is Tortiya and the main tributaries include rivers Lopkoho, Solomougou, Lafigué, Badénou, etc. The study area enjoys a sudanian climate with two contrast seasons: a rainy season from May to October and a dry season from November to April. The mean annual rainfall is estimated to 1230

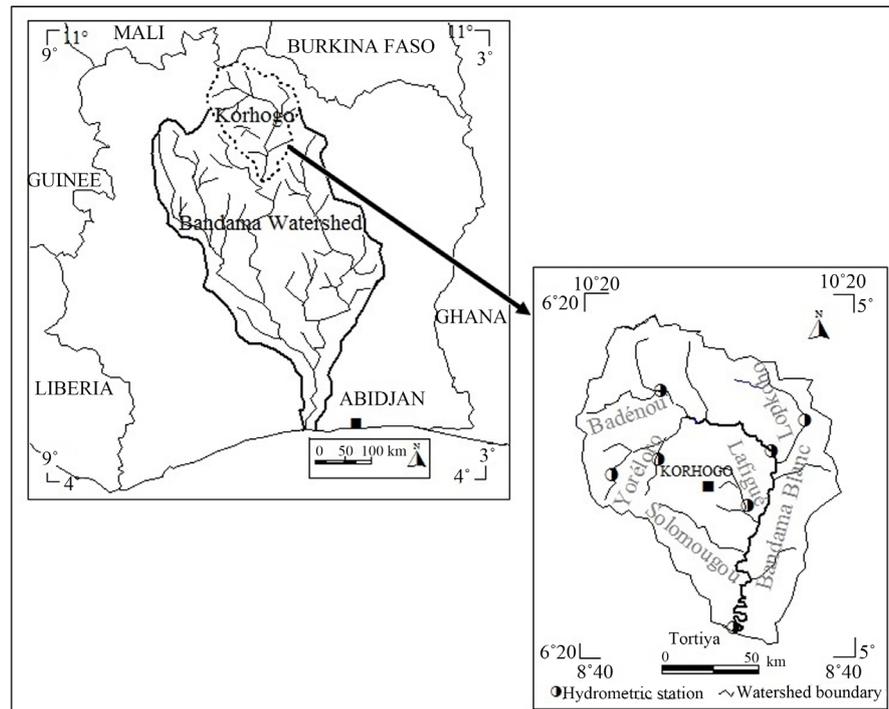


Figure 1. Location map of the study area (Soro, 2014).

mm for 1950-2000 period (Soro, 2014). Hydrologic regime is calqued on rainfall. Mean annual temperature is 26.6°C for 1972-2000. However, the highest values occur in dry season with a peak on March (29.5°C) and the lowest in rainy season with the minimum on August (24.7°C) (Figure 2). Rainfall and temperature evolutions are opposite. When rainfall increases, temperature decreases. Average monthly relative humidity ranges between 35% and 79% and insolation values vary from 160.6 hours in July to 273.8 hours in January.

The basin is underlined mainly by the Lower Proterozoic and Archean formations (Arnould, 1961). The Proterozoic formations are divided in two parts: Eburnean complex and Birimian (Figure 3). The Eburnean consists of granitoid type with granite, granodiorite and Gabbro. The Birimian is composed of schists, grey-wackes, metasediments and metavulcanites. Archean formations are migmatites.

2. Materials and Methods

2.1. Sample Collection

Field samples points were selected, taking in consideration the availability of boreholes and/or wells in the area. In all, thirty-five (35) boreholes and hang-dug wells were sampled at various locations (Figure 3) in December 2012. The depth of the boreholes ranged between 30 m and 60 m and those of wells are approximately sixteen (16) to twenty (20) meters. The location of the sample points were taken with the aid of a Global Positioning System (GPS) Garmin Type 12 receiver. All the samples were collected in 0.5 l using pre-cleaned polyethylene bottles. At first the bottles were rinsed by the spring's waters several times and

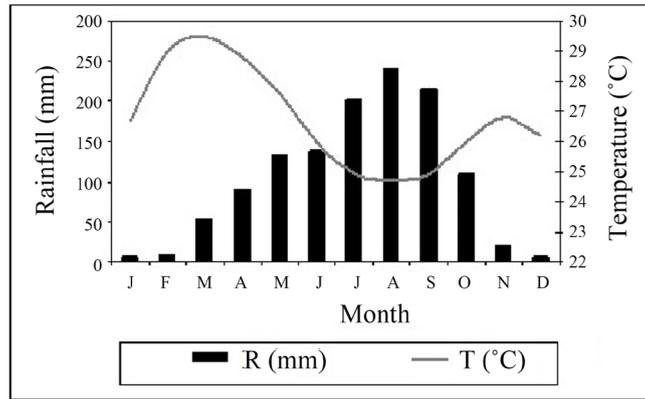


Figure 2. Ombro-thermal diagram of Korhogo synoptic station from 1972 to 2000.

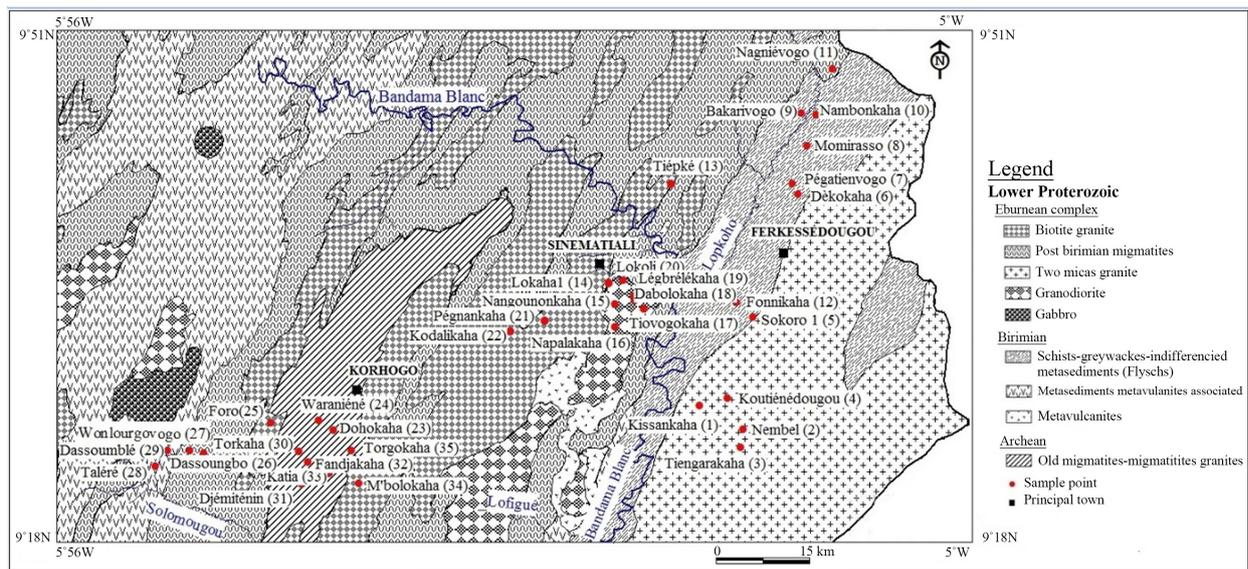


Figure 3. Map showing the sampling area and geological formations.

then collect the water. The bottles are completely filled with water to avoid air bulls. This was carried out to ensure that the samples bottles were free from contaminants. At the sampling points, the boreholes were pumped in order to purge the aquifer of stagnant water to acquire fresh aquifer water samples for analysis. Collected samples were preserved at lower temperature in an ice chest containing ice blocks and transported to laboratory in short time.

For all samples, temperature (T°C), pH, electrical conductivity (EC) and Potential Oxidation Redox (ORP) were determined *in situ*. The material used is a Water Test, multi-parameters tool of HANNA type instruments serial No. 058663 which gives the four parameters cited. The absolute error for the measurement is estimated to ±0.2 pH for pH, ±5 mV for potential of oxydo-reduction (ORP), ± 2F.S for electrical conductivity and ±1°C for temperature.

2.2. Sample Analysis

Major ions (Ca²⁺, Mg²⁺, Na⁺, Cl⁻, NO₃⁻, HCO₃⁻) were analyzed by spectrophoto-

tometric method in laboratory of water chemistry of Institute National of Hygiene Public (INHP) of Abidjan using HACH DR5000 spectrophotometer. Whereas, K^+ , SO_4^{2-} and PO_4^{3-} were analyzed in the Center of Research Oceanology (CRO) using standard methods. The sulfates (SO_4^{2-}) were analyzed by nephelometric method. Potassium was analyzed by Atomic Absorption Spectrophotometer (AAS) and phosphates (PO_4^{3-}) by Murphy and Riley method.

2.3. Data and Methods

The analytical data obtained were processed for detailed geochemical study. Diagram software package was used for determining water types. It features a fully customizable database of physical and chemical parameters and it provides a comprehensive selection of analysis tools, calculations and graphs for interpreting water quality data base. Statistical parameters such as min, max, mean (average) and standard deviation (SD) were computed by using STATISTICA version 7 software. For ion exchange, we use the Chloro alkaline indices (CAI) suggest by Schoeller (1967) in Pazand & Hezarkhani (2012). It is calculated using Equation (1):

$$CAI = \left[Cl^- - (Na^+ + K^+) \right] / Cl^- \quad (1)$$

where Cl, Na and K concentrations are expressed in meq/l.

Water Chemistry

The analyzed ions were used to determine the process controlling the water chemistry in the basin based on Gibbs (1970) diagram. This diagram is based on three dominant processes: evaporation or crystallization, rock-dominance or weathering and precipitation. The reaction between groundwater and aquifer minerals has a significant role in groundwater quality which is useful to assume the genesis of water. The data points were plotted in this diagram and the domain where the points fall determines the dominant process. It is a graph of TDS

versus $\frac{Na^+}{Na^+ + Ca^{2+}}$.

3. Results and Discussion

3.1. Physico-Chemical Parameters and Groundwater Quality

Statistical summary results of hydrochemical parameters measured in the groundwater samples collected in December 2012 are listed in Table 1. Groundwater temperature is generally low and ranges from 26.70°C to 30.70°C with an average of 28.80°C. The pH of the groundwater varies from 3.20 to 6.90 and its average (mean) is 5.40. The lowest pH occurred at Dokaha new well and Waraniéné borehole meanwhile the highest value was obtained at Dabolokaha borehole (Sinématiali area). The WHO recommended limit for potable water is 6.5 - 9.5. About 85.7% of the samples (30) fall outside the recommended range while 14.3% fall within the range. The acidic character of groundwater is conformity to the studies carried out by Savané (1997) in Odienné region and

Table 1. Statistical summary of the hydrochemical parameters in the study area.

Parameter	Minimum	Maximum	Mean	SD
T (°C)	26.70	30.7	28.80	1.01
pH (units)	3.20	6.90	5.40	0.95
EC (µS/cm)	77.00	553.00	250.30	108.70
ORP (mV)	21.00	266.00	147.70	65.80
Ca ²⁺ (mg/l)	4.00	56.00	18.11	12.66
Mg ²⁺ (mg/l)	0.00	55.00	15.31	15.59
Na ⁺ (mg/l)	0.00	26.00	6.93	7.57
K ⁺ (mg/l)	0.00	0.09	0.01	0.02
NH ₄ ⁺ (mg/l)	0.00	0.06	0.01	0.01
HCO ₃ ⁻ (mg/l)	5.00	215.00	77.00	49.19
Cl ⁻ (mg/l)	0.00	38.00	10.77	11.66
SO ₄ ²⁻ (mg/l)	0.60	47.24	9.70	11.80
PO ₄ ³⁻ (mg/l)	0.01	0.21	0.05	0.06
NO ₃ ⁻ (mg/l)	0.16	36.00	13.91	12.91

those of Faillat & Blavoux (1989) on ivorian fractured aquifers. These latter authors indicate that the pH values can decrease to 4 seek 3 in Côte d'Ivoire fissures aquifers. Acidic character of groundwater may be lied to excess quantity of free CO₂ present in the soil or to the water flow on substances called permutolits releasing the H⁺ ions (Jourda, 1987; Soro, 1987; Tapsoba-Sy, 1995; Oga, 1998).

One of the most effects of acidification of groundwater is corrosion. Acid groundwater can corrode plumbing system and solubilize metals in the soil or in the plumbing systems (Bertills & Bertil, 1995). According the studies of Knutsson (1994), the corrosion will also increase the copper content in drinking water, which may be a risk to the human health: infant diarrhea is suspected when the copper content in tap water exceeds 1 mg Cu l⁻¹ and fatal liver cirrhosis has been observed as an effect of elevated copper content in drinking water in several countries, for example Germany (Oskarsson & Strinnö, 1990) and India (Bhave et al., 1987).

Electrical conductivity (EC) values were generally low. Minimum and maximum values were respectively 77 µS/cm and 553 µS/cm with the mean value of 250.3 µS/cm. Major cations (Ca²⁺, Mg²⁺, Na⁺ and K⁺) were also generally low with Ca²⁺ and Mg²⁺ being the most dominants. Ca²⁺ and Mg²⁺ concentration ranges from 4 - 56 mg/l and 0 - 55 mg/l respectively with mean value of 18.11 and 15.31 mg/l. Bicarbonate (HCO₃⁻) is the most dominant anion with minimum and maximum values ranging from 5 to 215 mg/l.

The nitrate in the groundwater varied from 0.16 - 36 mg/l with a mean of 13.91 mg/l. These values don't exceed the drinking water guideline value of 50 mg/l according WHO. Even though it has been observed that igneous rocks

contain small amounts of nitrate (Daviest & Dewiest, 1966) cited by Gibrilla et al. (2010), most nitrate in water comes probably from fertilizers, nitrification by leguminous plants and animal excreta. Nitrogen is an essential component of protein hence occurs in all living organisms. When these material decay through microbial activities, the complex protein changes through amino acid to ammonia, nitrite and finally nitrate. The nitrate produced may leach the groundwater. Nitrate ion concentration in excess in drinking water creates several problems (Mishra et al., 2005) in Ghislain et al. (2012) like cyanosis, tumors goiter, oral cancer, lymphoma and dispnea. Nitrate contaminated water supplies carries the risk of methaemoglobinaemia (blue-baby syndrome) and stomach cancer. The main pollution risk for the aquifers is vertical infiltration of precipitation and flushing of pollutants from the soil. NH_4^+ and PO_4^{3-} were observed to have generally low concentration ranging from 0 - 0.06 mg/l and 0.01 - 0.21 mg/l respectively.

3.2. Hydrochemical Facies

Groundwater samples are grouped into facies depending on the dominant ions present. The Piper trilinear plot of groundwater is shown in Figure 4. The majority of the groundwater samples including boreholes (F), modern well (PM) and traditional well (PT) on the study area are characterized by Ca-HCO₃ (48.57%) or Ca-Mg-HCO₃ (31.43%) water type. Near, the second group which occupies about 17.14% of the samples is Ca-Mg-Cl water type. One sample (n° 22) corresponding to traditional well is Na-Cl water type.

In general, the study area groundwater is bicarbonate (HCO₃) type. This result is similar to those of many researchers like Biémi (1992), Soro (1987, 2002),

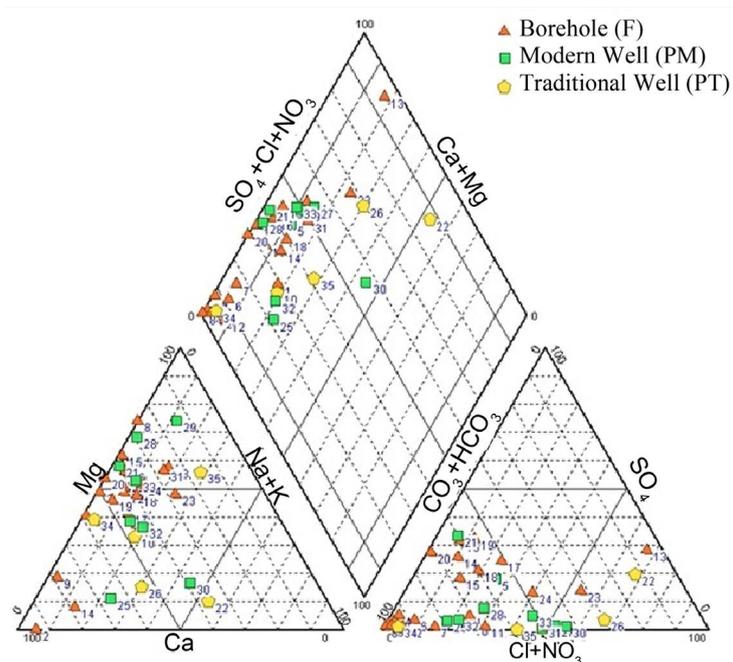


Figure 4. Piper plot for the groundwater samples of High Bandama Watershed.

Faillat & Blavoux (1989) who are noted the dominance of HCO_3^- ion in hard rock terrain of Côte d'Ivoire. Some similar results are been obtained in Burkina Faso by Yameogo (2008).

3.3. Hydrochemical Processes

• Compositional Relation

Since Ca^{2+} , Mg^{2+} , Na^+ , K^+ , HCO_3^- , Cl^- , SO_4^{2-} , NO_3^- are the observed solutes in the groundwater, an examination is made using relation between ions to account for their sources or origin. The chemical data of the groundwater samples are plotted on $\text{Ca}^{2+} + \text{Mg}^{2+}$ versus $\text{HCO}_3^- + \text{SO}_4^{2-}$ (Figure 5). In fact, the plot of $\text{Ca} + \text{Mg}$ versus $\text{SO}_4 + \text{HCO}_3$ is a major indicator to identify ion exchange process activated in the study area (Srinivasamoorthy et al., 2008). The majority of samples fall above the equiline (1:1) (black line) indicating predominance of alkali earth or excess calcium and magnesium in groundwater exchanged with sodium from aquifers materials. Nevertheless, some samples fall in $\text{HCO}_3 + \text{SO}_4$ indicating the ion exchanges process which may be due to excess bicarbonate (Figure 5).

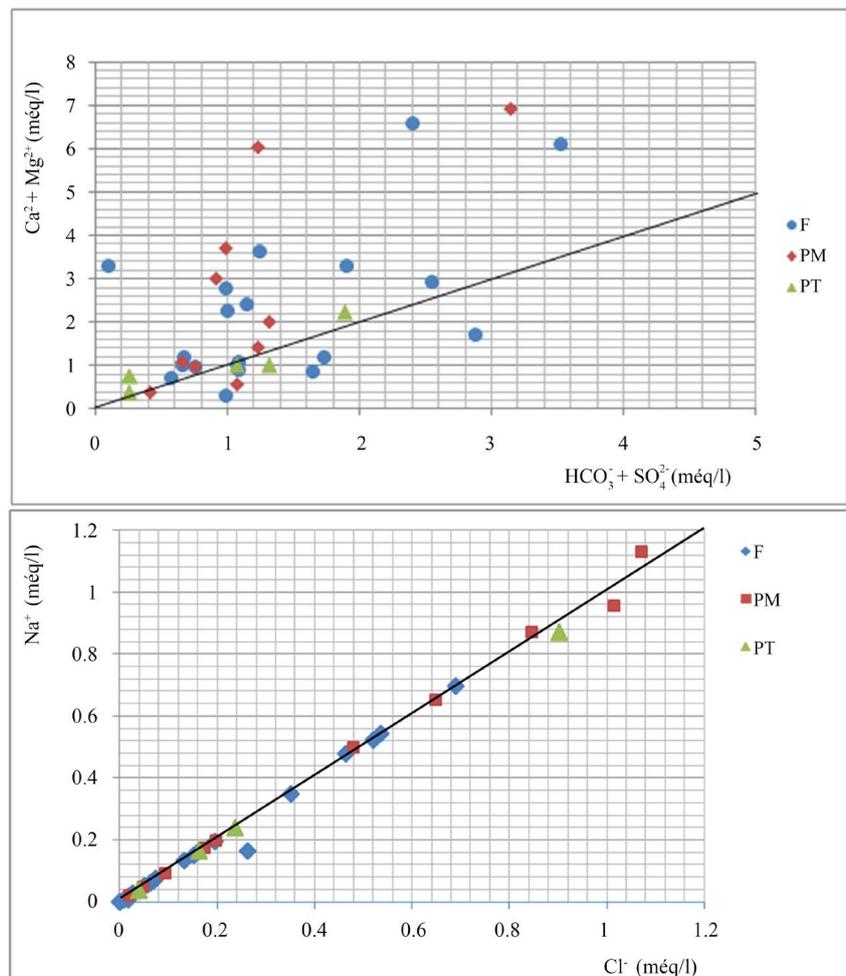


Figure 5. Relationship between $\text{Ca} + \text{Mg}$ vs $\text{HCO}_3 + \text{SO}_4$ and Na vs Cl .

The plot for Na versus Cl (Figure 5) shows that majority of samples fall on the equiline (1:1). The Na/Cl relationship has often been used to identify the mechanism for acquiring salinity and saline intrusion (Sivasubramanian et al., 2013). Sodium and chloride show a good correlation indicating groundwater are probably controlled by water-rock interaction. But for some authors like Li et al. (2018), when Na/Cl molar ratio is approximately equal to 1, it means that Na and Cl come from halite (NaCl), whereas a ratio greater than one is commonly interpreted as Na release from a reaction during silicate weathering. But Na and Cl may have some other source. According the study of Sako et al. (2018) in the northwestern Burkina Faso, atmospheric deposition (dust and rainfall) and decomposition of organic matter may be a source of Cl.

- *Cation-exchange*

Figure 6 shows the distribution of Chloro alkaline indices (CAI) in the study area. The majority of samples (66.67%) show negative values for indices whereas 33.33% are positive values. When the indices are positive, we talk about direct exchange and indirect exchange in opposite case. Positive indices mean that Na and K from groundwater are exchanged with Ca and Mg from the host rock. Most samples with negatives indices suggest that Ca and Mg from the groundwater are exchanged with Na and K from host rock.

- *Gibbs diagram*

In additional to Piper diagram and compositional relation, Gibbs diagram was also used to gain better insight into hydrochemical processes such as precipitation, rock-water interaction and evaporation on groundwater chemistry in the study area (Figure 7). The graph of TDS versus $\frac{Na^+}{Na^+ + Ca^{2+}}$ for the 35 data points indicates that groundwater within the watershed is located within the rock weathering field. This suggests that weathering and subsequent dissolution of the minerals present in the groundwater is the dominant process in the study area. In other term, it means that precipitation induced chemical weathering along with disso lution of rock forming minerals. In the literature, there are

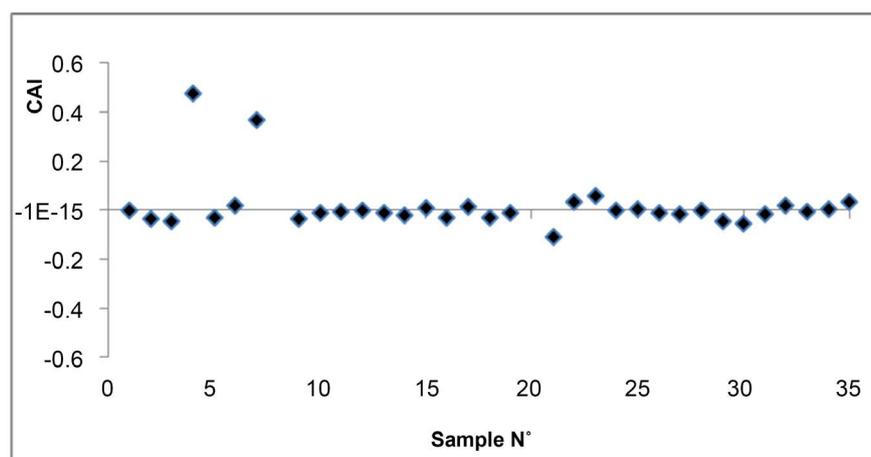


Figure 6. Distribution of Chloro alkaline indices (CAI) in the study area.

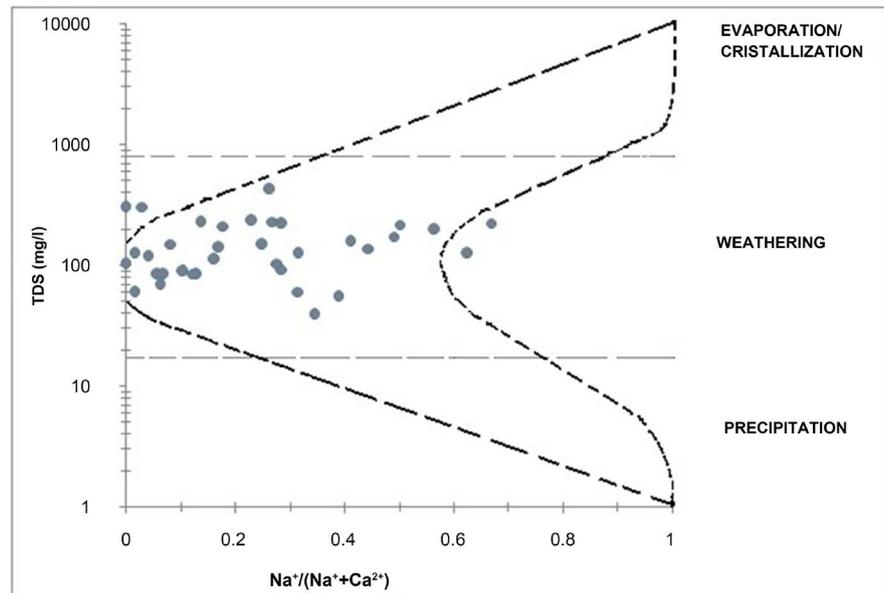


Figure 7. Mechanism controlling groundwater chemistry in the study area.

many types of Gibbs diagram. Aghazadeh et al. (2017), Adimalla & Venkatayogi (2018) used Gibbs diagram forms TDS versus $(Na + K)/(Na + K + Ca)$ and TDS versus $Cl/(Cl + HCO_3)$ to determine respectively mechanisms governing groundwater chemistry in the Ardabil area, a city in northwest of Iran and the groundwater chemistry evolution in semi-arid region of Basara, Telangana in south India. Their study reveals that weathering of rock (rock dominance) is the main control of groundwater chemistry. Moreover, Aghazadeh et al. (2017) show also in some of samples evaporation is influencing groundwater quality.

4. Conclusion

This study investigated the physico-chemical properties of the groundwater to understand the status of water quality and also the ions sources. The groundwater is acidic with pH values ranges from 3.20 to 6.90 and an average of 5.40. Electrical conductivity (EC) values were generally low. Minimum and maximum values were respectively 77 $\mu S/cm$ and 553 $\mu S/cm$ with the mean value of 250.3 $\mu S/cm$. Major cations (Ca^{2+} , Mg^{2+} , Na^+ and K^+) were also generally low. Ca^{2+} and Mg^{2+} are being the most dominants cations with concentration values ranges from 4 - 56 mg/l and 0 - 55 mg/l respectively with mean value of 18.11 and 15.31 mg/l. Bicarbonate (HCO_3^-) is the most dominant anion with minimum and maximum values ranging from 5 to 215 mg/l. In general, all parameters values are within the WHO guideline values and groundwater quality is good for drinking.

Four types of water were identified which are Ca- HCO_3 (48.57%), Ca-Mg- HCO_3 (31.43%), Ca-Mg-Cl (17.14%) and Na-Cl (2.86%) in which Na-Cl type was observed in one sample. The study area groundwater is generally bicarbonate (HCO_3^-) type. Compositional relation carried out by plots of Ca + Mg versus

HCO₃ + SO₄ and Na versus Cl showed that excess of Ca and Mg from groundwater is exchanged with Na and K from aquifer materials. The calculation of Chloro Alkaline Indice (CAI) confirms the results of Ca + Mg versus HCO₃ + SO₄ plot. It shows that the majority of groundwater samples (66.67%) with negative values of CAI exchange their ions Ca and Mg with the ions Na and K from host rock. In reverse, 33.33% of groundwater samples are exchanged their ion Na and K with ions Ca and Mg from aquifer materials.

Gibbs diagram demonstrates that weathering or rock dominance is the dominant process responsible of water chemistry in the study area. Further investigation on the rock-water interaction was indicated the dominance of silicate weathering on the other processes in contributing the ions such as Na, Ca, Mg, HCO₃, etc. This study provides a baseline for the groundwater chemistry in the High Bandama region.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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