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Assessment of Hydrogeochemical Processes Affecting Groundwater Quality in the Eocene Aquifer of Diourbel, Senegal

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Abstract

Groundwater quality is an important factor in determining the health of the population and the development of various human activities. However, its hydrogeochemical characteristics and water quality in the Eocene aquifer remain poorly documented in the Diourbel region, in a context where the superficial layer is not very productive and the deep layer, brackish. To identify the presence of various hydrogeochemical processes and the factors determining groundwater quality, an investigation was conducted in the Eocene aquifer, using statistical methods, binary diagrams, the chloride-alkali index, and the saturation index. The results show that the pH of the groundwater was neutral to slightly alkaline (ranging from 6.7 to 8.3) and high salinity in some areas due to the presence of trapped seawater (TDS ranged from 276 to 2964 mg/L). The Piper Diagram shows three majors water types: Ca-HCO_3^- (73%), Mixed-HCO_3^- (13%) and Na-Cl (5%). The concentrations of alkaline earth minerals (Ca^{2+} + Mg^{2+}) exceed those of alkalines (Na^+ + K^+) and bicarbonate (HCO_3^-) dominates the majority of groundwater samples. Statistical approach shows an affinity between alkaline and alkaline-earth elements, suggesting a common origin, and a lesser affinity between nitrate (NO_3^-) and chloride (Cl^-), indicating a marine origin of Cl^-. Geochemical diagrams reveal that carbonate mineral dissolution/precipitation and reverse ion exchange processes are the most important factors governing groundwater chemistry, confirmed by the binary diagrams and the chloro-alkaline index. This study guarantees a solid basis for the knowledge of geochemical processes at the origin of water mineralization. It represents a starting point for good resource management measures.

Keywords

Hydrogeochemical Processes, Groundwater Quality, Diourbel, Senegal

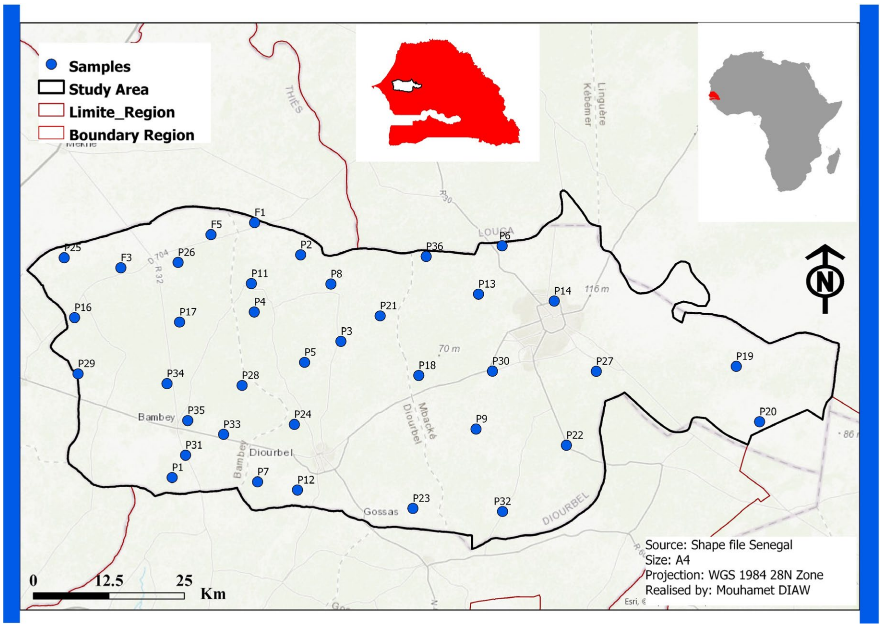
1. Introduction

Groundwater is an essential resource for economic and social development worldwide and constitutes one of the most important components of the natural environment. According to Nickson et al. (2005), a third of the world's population uses groundwater for drinking water supply. In developing countries, particularly in semi-arid to arid areas, population growth associated with increased industrial activities, the low rainfall and the quality of surface waters leads to a systematic use of groundwater to meet the water needs of the population, which leads to an overexploitation of groundwater and a gradual degradation of its quality. This deterioration of groundwater quality is a major concern for the authorities responsible for the drinking water supply. Indeed, this degradation affects not only water quality but also the health of populations as well as economic activities. Groundwater quality degradation can be linked to natural factors such as the natural weathering process of rocks and minerals, ion exchange reactions, oxidation-reduction reactions during the infiltration of water, saline water intrusion, evapotranspiration (Jeen et al., 2001; Kim et al., 2003; Kumar et al., 2009; Lee & Song, 2007; Li et al., 2013; Nematollahi et al., 2016; Varol & Davraz, 2014) and anthropogenic activities such as sewage effluent and fertilizer applications, unregulated urbanization, household and livestock feedlots (Diedhiou et al., 2012; Kumar et al., 2009; Vetrimurugan et al., 2013). In recent years, several studies have been carried out to determine temporal and spatial variation of groundwater quality well as to identify the main factors that influence water quality (Subba Rao, 2006) assessed the impact of seasonal variation of water quality on irrigation and human health. In this study, conventional hydrochemical methods combined with water quality assessment techniques (Residual Sodium Carbonate, Total Hardness) are used as tools to assess groundwater resources. Their results show that groundwater quality is controlled by evaporation-dominance and most of groundwaters samples, especially in the post-monsoon period are not suitable for drinking. For irrigation purposes, their results indicate that the majority of the groundwater samples are unsuitable for irrigation in post-monsoon compared to that in pre-monsoon (Li et al., 2013). It evaluates the groundwater quality for irrigation purposes and its hydrogeochemical evolution mechanisms in China (Pengyang County). The results of their study indicate that groundwater is generally suitable for agricultural use and groundwater quality is mainly controlled by mineral weathering and ion exchange processes. Zhang et al. (2022) illustrates the hydrogeochemical characteristics and the mechanism of evolution, by integrating multivariate statistical methods and hydrogeochemical methods. In addition, the water quality entropy index (EWQI) and water quality indices combined with spatial analysis were used to assess the suitability of groundwater for drinking and irrigation purposes and analyze the spatial variation of water quality. The results show a groundwater chemistry characterized by representative water types, ranging from freshwater to high salinity waters. The main control factors of hydrogeochemistry revealed by the Gibbs diagram were evaporation and water-rock interactions. In addition, the Gaillardet diagram, chloro-alkaline indices, binary diagram and saturation index indicate that silicate and evaporite alteration, ion exchange, halite dissolution, gypsum and anhydrite are responsible for the hydrogeochemical process (Benam-Beltoungou et al., 2025). We evaluated the quality of groundwater for drinking water and agricultural uses, analyzed the spatial variations of groundwater pollution and identified the hydrochemical processes influencing water chemistry in the Dakar region (Senegal). However, little work on this aspect has been done so far in the rural area on the intermediate aquifer of Eocene in the region of Diourbel, Senegal. Indeed, the study area is located in the center of Senegal with an economic activity based on peanut cultivation, but the availability of water in quality and quantity limits all socio-economic activities. This study aims to elucidate the predominant hydrogeochemical processes governing groundwater mineralization and initiate appropriate management of this resource in the Eocene aquifer of the Diourbel region and provide quality water to the population, where the superficial aquifer is not very productive and the most productive aquifer (Maestrichtian) is brackish in this region. To achieve this, a combined approach using a set of complementary tools was adopted. First, we used descriptive statistics for proper identification of affinities between chemical elements. Secondly, conventional hydrochemistry, with Gibss diagram, saturation index, chloralkali index and binary diagrams, were used to identify the main processes responsible for water mineralization.

2. Study Area

2.1. Location and Climate

The present study area (Diourbel region) is located in central part of Senegal (call “groundnut basin” area). It lies between 14˚30 and 15˚ North latitude and 15˚40 and 16˚40 West longitude and covers an area of 4769 km^2 (ANSD, 2013). It is bordered to the east by the Kaffrine region, to the west by the Thiès region, to the north by the Louga region, and to the south and southwest by the Fatick region (**Figure 1**). According to the National Agency of Statistics and Demography (ANDS) projections for the year 2025, the Diourbel region will be the third most populated region in Senegal behind Dakar and Thiès, with 2,179,594 inhabitants (ANSD, 2014). The Diourbel region is characterized by a strong agricultural activity which is largely dependent on rainfall. Groundnut production, which is highly dependent on rainfall, is highly variable from one year to another. The climate of the study area is Sudano-Sahelian and is characterized by a long dry season and a short rainy season occurring only three to four months (July, August and September). The maximum rainfall is observed in the month of August with a cumulation of 209 mm compared to 94 mm and 153 mm, respectively for the months of July and September. The maximum monthly average temperature increases during the dry season, reaching up to 40˚C.



Source: Shape file Senegal
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Figure 1. Location of the Study area with groundwater sampling sites.

2.2. Geological and Hydrogeological Setting

The study area is part of the Senegal-Mauritanian sedimentary basin, which covers an area of 340,000 km^2 and extends approximately 1300 km from Cap Blanc in the north (Mauritania) to Cap Roxo in the south (Guinea-Bissau). Its greatest width is 550 km at the latitude of Dakar. The geological formation shows a succession composed of clay and sand from the continental terminal (CT), marls and limestones from the Eocene (Eo) and the Paleocene (Pa), and quartz sands and sandstones of Maastrichtian (Ma). In the study area, the Eocene is essentially formed of marly limestone, limestone, and nummulites (Sarr, 2000). At the beginning of the Lower Eocene (Ypresian), a new transgression occurred, extending the marine basin to its greatest extent to the east and allowing the deposition of a series dominated by attapulgite clay, rich in flint, glauconite, and phosphate at its base, becoming more marly toward the top and interspersed with clayey limestone (Diaw, 2018; Sarr, 2000). At the beginning of the Middle Eocene, following the tectonic deformation caused by the collision of the African and European plates, the sea began to recede, leaving behind alternating layers of limestone and shell-rich marl (Castelain et al., 1965 in Roger et al., 2009). The Upper Eocene marks the period of sea retreat, during which only clay facies indicate detrital sedimentation. The W-E geological cross-section (**Figure 2**) obtained from the drilling data confirms that the Eocene is mainly composed of limestone, marl, marlylimestone, and the presence of silex, especially. The hydrogeology of the Diourbel region is characterized by the presence of several types of aquifers: the shallow aquifers, which include the CT and quaternary aquifers, which are very few exploited in the region, the intermediate aquifers, which include the Paleocene and Eocene aquifers, and the Maastrichtian, which constitutes the deep aquifer. The Eocene aquifer is mainly exploited by borehole and the water level of aquifer varies between 10 and 70 m (Diaw, 2018). The piezometric level varies between −26 to 25 m compared to IGN zero (Diaw, 2018). The waters flow from East to West, with one side of more than 20 m, characterizing an area susceptible to infiltration or rising of the water table (Diaw, 2018). The thickness of the Eocene aquifer increases from East to West and varies between 80 and 225 m (Northwest) with an average value of 150 m (Diaw, 2018). The mean transmissivity values of the Eocene aquifer vary from 2×10^{-5} to 1×10^{-3} m^2/s.

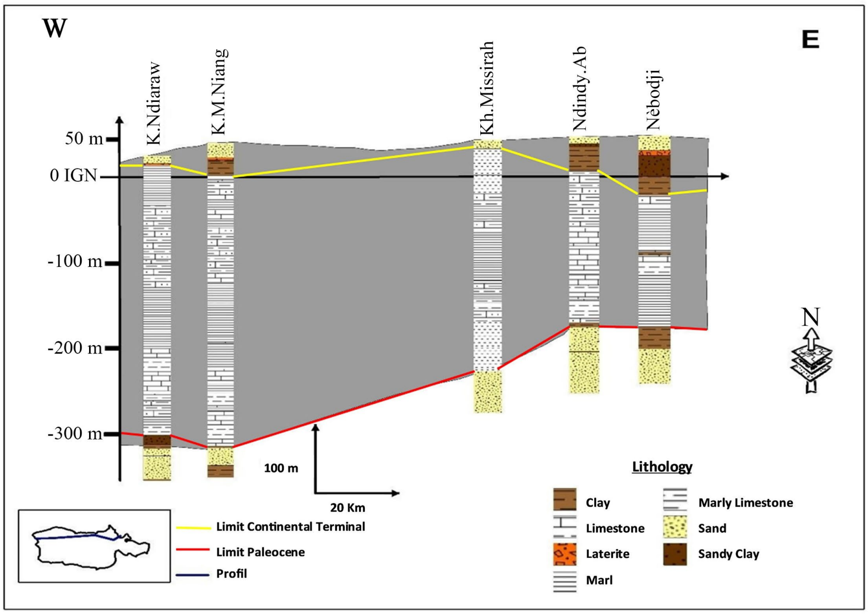

Figure 2. Geological section of the study area.

3. Groundwater Sampling and Analytical Methods

During October 2017 (post rainy season), a total of 37 groundwater samples were collected in polyethylene bottles of 250 mL on a sampling network, consisting of dug wells and boreholes, distributed throughout the study area. Standard protocol of water level measurement first followed by purging boreholes and dug well to representative groundwater samples was applied prior sampling. However, before sampling, the bottles were rinsed respectively with distilled water and then twice or three times with water to be collected and then the bottles were filled. At each dug well or boreholes two groundwater samples were collected and stored in two polyethylenes bottles. One of the bottles was acidified with HCl to pH~2 for cations determination. The other bottle for anions analysis was kept unacidified. Electrical conductivity (EC), pH and Temperature (˚C) were directly measured in the field using a multi-parameter probe WTW Multi 3630 IDS portable devices which was previously calibrated. After sampling, groundwater samples were immediately sealed and transported to the laboratory.

In the laboratory, groundwater samples were filtered through 0.45 μm cellulose membrane to retain suspended elements and colloids. The analysis of major ions (Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, Cl^-, SO_4^{2-}, NO_3^-) and selected minor ions (Fe^{2+}, F^-) was performed at the hydrochemistry laboratory of the Geology Department at University Cheikh Anta Diop, Sénégal. Dionex DX 120 chromatography system equipped with an automatic sampler, an AS4 column for anions (except HCO_3^-, which was determined via titration) and a CS12 column for cations (measurement precision of 3%) were used for major ions. Minor elements such as Fe^{2+} and F^- were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES). Data accuracy was verified by calculating the charge balance error (CBE) (Equation (1), as recommended by Hounslow (2018). All samples had a CBE within the acceptable limit of ±5%.

$$\text{CBE}(\%) = \frac{\sum \text{cations} - \sum \text{anions}}{\sum \text{cations} + \sum \text{anions}} \times 100 \quad (1)$$

The evaluation of geochemical stability is helpful for estimating groundwater chemistry evolution as well as associated main reactions (Diaw, 2008; Srinivasamoorthy et al., 2014; Ledesma-Ruiz et al., 2015; Emvoutou et al., 2018). It can be computed using the saturation index, SI = logIAP/KS, which result from comparison of the ion solubility product KS of minerals to the corresponding ion activities products in groundwater (IAP). Hence, the SI evaluates the equilibrium between minerals and groundwater. The values of saturation index (SI) were obtained through the hydrochemical software Diagram from the University of Avignon (France). The variations in ionic concentration were calculated, analyzed, and interpreted to gain a better understanding of the hydrochemical processes taking place in the aquifer. These processes were identified using a statistical approach and binary diagrams (Gibbs, Chloro-alkalin) highlighting the possible origin of the mineralization of water in Eocene aquifer. Data processing was carried out using Origin Pro, Statistica 7, ArcGIS 10.4 software and Python (Jupyter).

4. Results and Discussion

4.1. Hydrogeochemical Characteristics of Groundwater

Chemical characteristics of groundwater are mainly dependent on the interaction of rock and water along with geochemical processes occurring in the aquifer system (Mallick et al., 2018).

The physico-chemical data for the analyzed groundwater samples of the study area are given in **Table 1**. The statistical summary of groundwater samples is presented in **Table 2**. Electrical conductivity (EC) measures the salt concentrations of water and indicates of ionic concentrations. High electrical conductivity (EC) in water samples would result from leaching, dissolution of aquifer material or mixing of salt sources or a combination of these processes (HEM, 1985). EC of groundwater in the Eocene aquifer ranged from 390 to 4750 µS/cm with a median value of 915 µS/cm. According to WHO (2017), 1500 µS/cm is the allowable EC threshold in drinking water. Ten (10) samples (27%) have an EC > 1500 µS/cm, which can be the result of a set of hydrogeochemical processes and anthropogenic processes or marine contamination.

The pH values of groundwater sampled in the Eocene aquifer ranged from 6.7 to 8.3 with a median value of 7.5, indicating groundwater is slightly alkaline. According to World Health Organization (WHO) standards (WHO, 2017). The pH values of all groundwater samples are within the WHO standards (6.5 - 8.5). In the Eocene aquifer 3 out of 37 have a pH value < 7 suggesting carbonate dissolution minerals.

Total dissolved solids (TDS) value ranged from 276 to 2964 mg/L with a mean value of 844.81 mg/L. High TDS values influence groundwater suitability for drinking and agricultural use. Based on (Benam-Beltoungou et al., 2025; WHO, 2011), the maximum acceptable concentration of TDS in groundwater for a domestic purpose is 500 mg/L, and the excessive permissible limit is 1.500 mg/L. In the study area, only 7 samples out of 37 (19%) have TDS values over the maximum acceptable concentration and 5 samples (13.5%) have TDS values above the permissible limit. Freeze and Cherry (1979) classify water into fresh (TDS < 1000 mg/L), brackish 1000 < TDS > 10,000 mg/L), saline (10,000 < TDS > 100,000 mg/L) and brine (>100,000 mg/L) categories based on TDS concentration. Based on this classification, 81.1% of groundwater in the study area belongs to freshwater and the remaining 18.9% to brackish water categories.

The chemical composition of groundwater samples is presented in **Table 1**. Based on mean values of major ions in groundwater, the relative abundance of major cations and anions in collected groundwater samples was, respectively, in the order of $Ca^{2+} > Na^{+} > Mg^{2+} > K^{+}$ and $HCO_3^- > Cl^- > SO_4^{2-} > NO_3^-$. Calcium ($Ca^{2+}$) and bicarbonate ($HCO_3^-$) were, respectively, the dominant cation and anion, contributing 52% of total cations and 58% of total anions in groundwater samples. Calcium (Ca^{2+}) and magnesium (Mg^{2+}) are common elements in groundwater. The measured concentrations of Ca^{2+} in groundwater samples ranged from 41.6 to 232.04 mg/L with a median value of 96 mg/L. The permissible limit of Ca^{2+} concentration in groundwater is suggested by WHO (2011) is 200 mg/L. In the present study, the majority of groundwater samples have Ca^{2+} concentration under the permissible limit except for three samples (P1, P13 and P14) which have higher Ca^{2+} concentration exceeding the permissible limit for drinking purposes. The Mg^{2+} concentration of groundwater ranged from 6.3 to 183.6 mg/L with a median value of 33.5 mg/L. According to the WHO standard (30 mg/L), twenty-one (56.8%) have magnesium content higher than the maximum permissible limit. Sodium (Na^{+}) concentration in groundwater of the study area ranged from 4.6 to 576.6 mg/L with a median value of 39.1 mg/L. Based on the permissible limit of Na^{+} concentration in groundwater suggested by WHO (2017) (**Table 3**). Most of the groundwater samples are well within the permissible limit except for fourth (4) groundwater samples (P1, P13, P17, P36) which exceed the permissible limit. Potassium (K^{+}) content in groundwater is very low compared to the sodium concentration. The excess content of Na^+ over K^+ is due to the greater resistance of potassium to chemical weathering and its adsorption on clay minerals. K^+ concentrations, in the study area, ranged from 1.34 to 30.17 mg/L with a median value of 4.5 mg/L. In the study area, except one sample which has 30.17 mg/L, K^+ concentration is well within the maximum permissible limit.

Bicarbonate (HCO_3^-) was the most abundant anion in groundwater samples. The concentration of HCO_3^- in the study area ranged from 67.1 to 610 mg/L with a median value of 311 mg/L. Dissolution of carbonate and/or alumino-silicate rocks with a secondary contribution from dissolution of CO_2 gases, produced by the biodegradation of organic matter and root respiration, is considered the primary source of HCO_3^- in the groundwater (Singh et al., 2013). In fact, the produced soil CO_2 combines with rainwater to form bicarbonate.

Chloride (Cl^-) is the second most abundant anion of groundwater in the study area. The chloride content in groundwater can be linked to the dissolution of certain rock minerals such as halite, to the marine intrusion process in coastal aquifers but also to anthropogenic pollution in agricultural and high-density populated areas. In the present study, the chloride concentration ranged from 21.6 to 1447.91 mg/L with a median value of 85.5 mg/L.

According to the WHO standard (250 mg/L), six groundwater samples (16.22%) have chloride content exceeding the WHO permissible limit.

The concentration of sulfate (SO_4^{2-}) ranged from 0.92 to 485.8 mg/L with a median value of 43.7 mg/L. Drinking water with a SO_4^{2-} concentration higher than the WHO standard (250 mg/L) can lead to the appearance of unpleasant taste and corrosion of distribution pipes, while water with SO_4^{2-} concentrations higher than 500 mg/L may cause risk to human health such as gastrointestinal disorders (WHO, 2017). Based on the standard limit, The SO_4^{2-} concentration of all the groundwater samples, except for three groundwater samples (P17, P18, and P20), are well within the standard guideline value.

Nitrate (NO_3^-) is, next to bicarbonate, Cl^-, and SO_4^{2-} , the fourth most abundant anion in the groundwater of the study area. Its contents, vary from 0.41 to 577.81 mg/L with a median value of 2.6 mg/L. Except for Dug well P3, P13, P14, P22, P27, and P32, which have respectively 62.56 mg/L, 577.81 mg/L, 181.02 mg/L, 119.8 mg/L, 66.4 mg/L, and 120.09 mg/L, all the other groundwater samples have NO_3^- concentration lower than the recommended desirable limit of 50 mg/L for drinking water.

Fluoride (F^-) is one of the primary trace elements in groundwater typically occurring as a natural constituent. It is an important element required for humans to prevent dental caries. However, high concentration of fluoride can lead to the deterioration of human health (Narsimha & Rajitha, 2018). Fluoride in water is mainly derived from the weathering of fluoride-bearing rock-forming minerals like muscovite, biotite, fluorite, fluoro-apatite (Singh et al., 2013) or weathering and deposition of atmospheric volcanic particles (Amiri et al., 2015). In the study area, fluoride has the lowest content and derived for fluoro-apatite. The concentration of fluoride ranged from 0.08 to 0.48 mg/L with an average value of 0.3 mg/L. The recommended value of fluoride in drinking water is 1.5 mg/L (WHO, 2011). According to the WHO standard, all the groundwater samples, in the study area, are below the drinking water desirable limit. In the Mbour-Thiès-Diourbel-Fatick perimeter, highly fluorinated Paleocene waters circulate in a paleokarst. They are charged under a quasi-continuous phosphate level marking the base of the Eocene. In sedimentary reservoirs, fluorapatite plays an essential role in mineralization through its dissolution in water thus releasing fluorine (Travi, 1993). The presence of fluoride may result from contamination by fluorinated water, due to vertical exchange between the highly fluorinated waters of the Paleocene and those of the Eocene (Sarr, 2003), along with tectonic deformation caused by the collision of the African and European plates.

In aquifers, several hydrogeochemical processes, natural and anthropogenic factors can cause a spatial change in the chemical composition of groundwater inducing the appearance of several water types. The Piper diagram (Piper, 1944) diagram has been widely used since it is very useful in determining relationships of different dissolved constituents and classification of water based on its chemical characters (Singh et al., 2012). Based on the chemical composition of cations and anions in groundwater samples, the hydrochemical types of groundwater in the study area were classified into three main water types. These are Ca^{2+}- HCO_3^- type, which constitute the dominant water type in the study area (73%), Mixed-HCO_3^- type, which the second most important water type (13.5%), Mixed Cl^- and Ca^{2+}-Cl^- type observed, respectively, in only two dug well (5%) (**Figure 3**).

Table 1. Major and minor ions concentrations and related parameters of groundwater samples.

Libellé	Sample name	Aquifer	pH	EC	HCO_3^-	Cl^-	SO_3^{2-}	NO_3^-	F^-	Na^+	K^+	Mg^{2+}	Ca^{2+}	Fe^{2+}
P33	Baity	Eocene	7.9	1040	445.3	75.03	104.5	0.58	0.27	24.13	3.23	49.92	109.82	0.21
P12	Boundou	Eocene	7.36	1375	366	161.77	178.56	1.24	0.2	75.95	7.28	66.74	96.14	0.06
P27	Bousrah	Eocene	6.89	490	67.1	85.49	6.91	66.4	0.15	30.09	1.77	12.72	44.06	1.38
P2	Coky Ndiaguène	Eocene	7.24	997	244	135.1	105.23	0.81	0.31	45.77	7.23	45.96	68.35	0.11
P18	Darou Ndiaye	Eocene	7.88	1727	378.2	162.55	320.77	3.45	0.4	71.55	8.46	86.47	129.67	0.21
P22	Darou Salam Typ	Eocene	7.72	950	195.2	133.9	0.92	119.8	0.24	39.14	6.26	19.99	103.09	0.46
P4	diokoul 2	Eocene	6.91	1786	610	270.02	65.32	2.06	0.41	133.65	9.51	80.28	119.86	0.83
P28	Diorel	Eocene	7.92	1015	475.8	75.1	47.96	3.68	0.23	28.97	2.44	53.76	91.5	0.07
P25	Fassel	Eocene	7.7	760	152.5	94.5	98.7	0.72	0.18	46.53	4.53	9.27	88.74	0.14
P21	Gallé	Eocene	7.33	818	335.5	71.78	38.77	0.61	0.2	26.93	4.08	18.01	102.35	0.18
P3	Keur Awa Loumène	Eocene	7.21	900	253.15	80.83	57.7	62.56	0.35	41.65	6.82	33.93	68.14	0.14
P8	Keur Mousseu	Eocene	7.41	1070	366	136.2	92.08	0.63	0.3	73.82	6.21	44.75	76.34	0.07
F3	Kewré	Eocene	7.68	700	262.3	75.26	13.84	3.09	0.17	41.43	3.65	7.43	91.77	0.16
P31	Khandiar	Eocene	7.88	745	311.1	53.83	26.44	8.55	0.24	32.27	2.68	8.51	96	0.12
P23	Koba Diop	Eocene	8.09	754	268.4	72.06	23.86	17.16	0.19	30.83	3.87	17.10	79.86	0.31

Continued

F1	Lappe	Eocene	7.41	530	237.9	54.03	3.1	1.17	0.24	18.5	3.14	7.14	78.25	0.14
P36	Lougoul	Eocene	6.73	3680	128.1	1263.37	131.6	5.73	0.39	300.4	16.96	183.63	177.73	0.12
P16	Magagne	Eocene	7.83	1376	384.3	180.18	120.22	2.78	0.37	82.89	8.33	42.22	110.5	0.15
P6	Mbarane Thiam	Eocene	7.55	737	305	71.85	22.03	2.151	0.28	21.8	5.6	24.23	84.12	0.07
P34	Mbary 2	Eocene	7.95	1190	427	126	79.56	1.91	0.25	64.47	3.78	37.33	118.55	0.18
P13	Medina Touré	Eocene	7.15	2740	109.8	541.29	11.9	577.81	0.48	229.4	14.82	55.81	212.13	0.08
P11	Merina Dieng	Eocene	7.33	780	292.8	82.8	43.72	3.15	0.27	32.17	5.3	32.47	72.55	0.17
P26	Ndary Diop	Eocene	7.8	915	341.6	107.84	17.26	2.59	0.25	57.55	6.61	9.91	107.69	0.46
F5	Ndiégué	Eocene	7.79	681	305	57.59	5.42	0.65	0.23	20.32	3.02	9.72	96	0.05
P7	Ndjiss	Eocene	7.46	700	366	21.73	28.85	0.42	0.3	10.78	3.12	36.98	70.6	0.18
P20	Ngaraf Mbayène	Eocene	7.54	1480	274.5	135.7	285.24	3.7	0.3	141.35	8.1	13.72	125.29	0.12
P1	Ngascop	Eocene	7.29	4750	381.25	1447.91	165.12	1.78	0.41	576.62	30.17	135.96	224.2	0.07
P29	Ngogom	Eocene	8.1	700	384.3	28.8	3.47	5.12	0.14	6.92	1.89	26.94	87.65	0.49
P17	Peulh Ndiaye	Eocene	8.25	2370	427	287.74	485.8	2.59	0.45	233.17	11.42	65.71	163.84	0.28
P24	Sakal	Eocene	7.77	901	427	54.15	43.92	0.49	0.21	27.6	2.19	33.51	103.91	0.03
P19	Sandatou	Eocene	7.37	898	335.5	45	95.9	4.45	0.23	24.24	3.23	41.22	80.15	0.28
P35	Sandiara	Eocene	8	790	396.5	32.44	29.01	3.76	0.18	31.05	1.89	30.22	81.34	0.1
P30	Satte	Eocene	7.27	390	128.1	64.76	3.32	0.41	0.08	29.45	2.03	6.32	41.6	0.37
P5	Siguidiadji	Eocene	7.2	400	183	21.6	12.78	2.19	0.22	4.68	1.34	17.19	43.7	0.03
P9	Thialle	Eocene	8.26	946	298.9	126.34	79.81	1.36	0.29	69.14	6.69	38.63	70.41	0.21
P14	Touba Guédé	Eocene	7.33	2710	314.15	628.69	39.4	181.02	0.33	92.6	13.16	125.22	232.04	0.25
P32	Touba Mboul	Eocene	7.28	1110	198.25	150.21	26.6	120.09	0.33	25.55	2.92	25.70	137.7	0.07

Table 2. Descriptive statistics of physicochemical parameters.

Parameters	Number of samples	Means	Median	Minimum	Maximum	Standard déviation	WHO guideline values 2011 and 2017
TDS	37	844.81	651	276	2964	559.67	1000
EC	37	1240.57	915	390	4750	922.73	1500
pH	37	7.56	7.5	6.73	8.26	0.38	6.5 - 8.5
HCO_3^-	37	307.47	311.1	67.10	610	113.89	350
Cl^-	37	194.96	85.5	21.6	1447.91	309.01	250
SO_4^{2-}	37	78.8	43.7	0.92	485.8	100.74	200
NO_3^-	37	32.88	2.6	0.41	577.81	100.59	50
F^-	37	0.27	0.3	0.08	0.48	0.09	1.5
Na^+	37	76.85	39.1	4.68	576.62	107.19	200
K^+	37	6.32	4.5	1.34	30.17	5.51	12
Mg^{2+}	37	42.02	33.5	6.32	183.63	38.72	150
Ca^{2+}	37	105.02	96	41.6	232.04	45.86	200
Fe^{2+}	37	0.23	0.2	0.03	1.38	0.25	0.3
PO_4^-	37	0.19	0.1	0.09	1.89	0.31	

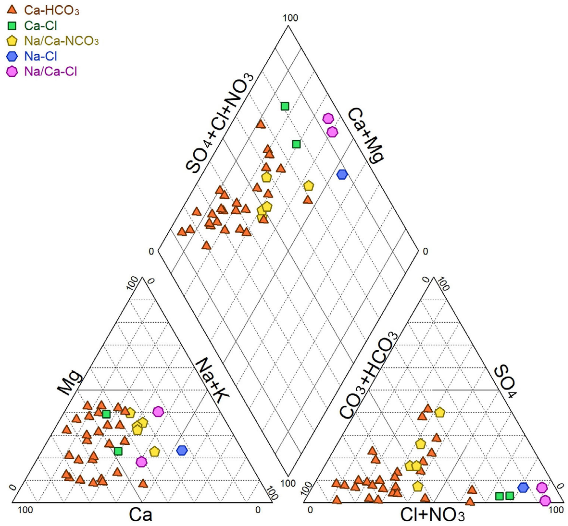

Figure 3. Piper diagram showing groundwater types of the Eocene aquifer.

4.2. Statistical Approach to the Groundwater Chemistry

The correlation matrix is a technique widely used for assessing the degrees of dependence between variables and measuring the relationships between dependent and independent variables. In this study. the correlation matrix was established using the Statistica software and RStudio to validate (**Table 3**). The results of the correlation matrix show strong positive correlation between EC/TDS and major ions Ca^{2+}, Mg^{2+}, Na^+, K^+. Cl^-, and F^- (**Table 3**). Moreover, significant positive correlation was observed between Ca^{2+} and Na^+ (r = 0.74); Ca^{2+} and K^+ (r = 0.79); Ca^{2+} and Cl^- (r = 0.77). between Ca^{2+} and Mg^{2+} (r = 0.71) and particularly between Na^+ and Cl^-. All the parameters used in the correlation matrix show a negative correlation with the pH, except for HCO_3^-, thus showing the role of pH in adding chemical elements in waters. Indeed, a significant correlation between pH and HCO_3^- with indicating that HCO_3^- participates in the alkalinity of the waters. High positive correlation coefficient Na^+ and K^+. between Na^+ and Cl^- and between K^+ and Cl^- may be due to the weathering of Na^+ and K-bearing minerals such as halite and sylvite, and clay minerals. It could also be attributed to the trapping of seawater as it receded during the Eocene. A weak positive correlation between Cl^- and NO_3^- (r = 0.22) shows that chloride concentrations are not anthropogenic. In fact. in the urban and peri-urban area. The correlation of high nitrate and chloride concentrations can be linked to anthropogenic pollution (Diedhiou, 2011). NO_3^- concentration ranged from 0.41 to 577.81 mg/L with an average value of 32.9 mg/L. In the study area majority of groundwater samples (83.8%) have NO_3^- concentration lower than the recommended desirable limit of 50 mg/L for drinking water indicating the suitability of this water for drinking use (Diaw, 2026). Only 6 works out of 37 have values greater than 50 mg/L. The weak correlation between Cl^- and NO_3^- indicates a marine origin of Cl. Indeed, The Eocene formation was marked by major tectonic phenomena that affected the sedimentary basin. The density of accidents is very high, but their reject is generally modest (Bellion, 1987). It will result in the general retreat of the sea but thus promote the trapping of seawater in certain parts of the upper horizons of the Eocene aquifer. Iron (Fe^{2+}) concentrations are low and negatively correlated with all variables, suggesting that they likely originate from corrosion of hydraulic equipment.

Table 3. Correlation matrix for physicochemical parameters of the study area.

Parameters	EC	TDS	pH	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	Cl^-	SO_4^{2-}	NO_3^-	F^-	Fe^{2+}
EC	1.00												
TDS	**0.99**	1.00											
pH	−0.26	−0.22	1.00										
Ca^{2+}	**0.89**	**0.88**	−0.11	1.00									
Mg^{2+}	**0.87**	**0.87**	−0.32	**0.71**	1.00								
Na^+	**0.93**	**0.94**	−0.23	**0.74**	**0.71**	1.00							
K^+	**0.95**	**0.95**	−0.28	**0.79**	**0.77**	**0.95**	1.00						
HCO_3^-	0.08	0.16	**0.41**	0.11	0.18	0.04	0.03	1.00					
Cl^-	**0.95**	**0.92**	−0.39	**0.77**	**0.85**	**0.91**	**0.92**	−0.09	1.00				
SO_4^{2-}	0.44	0.48	0.21	0.35	0.38	0.44	0.40	0.28	0.24	1.00			
NO_3^-	0.30	0.28	−0.25	0.49	0.11	0.19	0.27	−0.38	0.22	−0.18	1.00		
F^-	**0.71**	**0.73**	−0.19	0.68	0.62	0.62	**0.70**	0.19	0.55	0.51	0.39	1.00	
Fe^{2+}	−0.13	−0.14	−0.21	−0.19	−0.10	−0.09	−0.12	−0.09	−0.10	−0.12	0	−0.18	1.00

4.3. Processes Controlling Groundwater Chemistry

The spatial and temporal variation of groundwater mineralization depends on several factors that influence ionic concentration. Thus, the chemical composition of groundwater is generally controlled by lithological factors such as carbonate and gypsum dissolution, silicate hydrolysis, evaporite dissolution, evaporation and precipitation (Singh et al., 2013). Also, through anthropogenic activities such as irrigation return flow fertilizer, applications, wastewater, unregulated urbanization, households, and feedlots. The variation in the chemical composition of groundwater is strongly influenced by the water-rock interaction, which is generally the main source of ions in water. Gibbs' diagram widely used in several studies, makes it possible to distinguish three main natural mechanisms (evaporation dominance, rock dominance and precipitation dominance) that influence the chemical composition of waters. **Figure 4(a)** shows that the majority of groundwater samples fell in the zone of rock dominance suggesting that the chemical composition of groundwater is controlled by water-rock interaction, with the possible dissolution of minerals. Some samples in the study area were scattered outside the Gibbs model (**Figure 4(b)**) and might be affected by anthropogenic activities (Zhan et al., 2022). In order to clearly identify the main minerals dissolved in the groundwater system, several graphical plots were also used. Thus, the graph of $(Ca^{2+} + Mg^{2+})$ versus $(SO_4^{2-} + HCO_3^-)$ show that the majority of groundwater samples falling above and close to the equiline (1:1) suggesting an excess of (Ca^{2+}

+ Mg^{2+}) over (SO_4^{2-} + HCO_3^-) which might be derived from carbonate dissolution (**Figure 5(a)**). Ionic ratios such as Ca^{2+}/Mg^{2+} were generally used to identify the origin of calcium and magnesium in groundwater. If Ca^{2+} and Mg^{2+} were only derived from the dissolution of carbonates in the aquifer minerals (**Figure 5(b)**), a $Ca^{2+}/Mg^{2+} = 1$ suggests dissolution of dolomite, while a Ca^{2+}/Mg^{2+} ratio ranging between 1 and 2 indicates the dissolution of calcite (Sonkamble et al., 2012). Higher Ca/Mg molar ratio (>2) indicates the dissolution of silicate minerals, which contribute calcium and magnesium to groundwater (Kumar et al., 2006; Rajmohan & Elango, 2003; Yang et al., 2016). In the present study, 45.95% and 13.51% of groundwater samples have respectively a Ca^{2+}/Mg^{2+} ratio lying between 1 and 2 and close to 1 suggesting the occurrence of calcite and dolomite dissolution/precipitation as a likely source of these ions in groundwater. Moreover, 40.54% of groundwater samples have a Ca^{2+}/Mg^{2+} ratio > 2 indicating the contribution of the cation exchange. However, the saturation index (SI) of calcite and dolomite is saturated to oversaturated (**Figure 6(a)** and **Figure 6(b)**), indicating the existence of precipitation processes of these minerals. Only gypsum is undersaturated, indicating a contribution of Ca^{2+} and SO_4^{2-} (**Figure 6(c)**). The mean SI values for calcite and dolomite are 0.5 and 0.9 respectively, indicative of a slight oversaturation of groundwater with carbonate minerals, and the importance of carbonates dissolution in these waters (Lyu et al., 2019). This process is illustrated in **Figure 6(d)** where all samples, except for a few ones, showed saturation to oversaturation for calcite, which is consistent with the hydrogeochemistry of this area. Furthermore, the excess of Ca^{2+} and Mg^{2+} might be derived from other processes such as reverse ion exchange reactions.

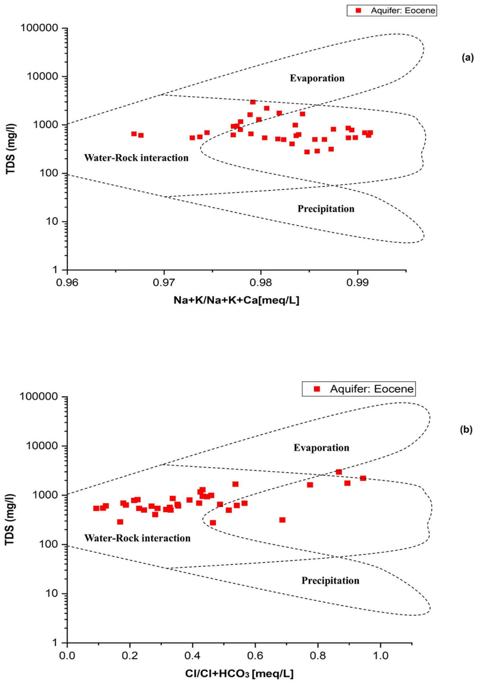

Figure 4. Mechanisms governing groundwater chemistry (a) TDS versus ($Na^+ + K^+$)/($Na^+ + K^+ + Ca^{2+}$); (b) TDS versus $Cl^-/(Cl^- + HCO_3^-)$.

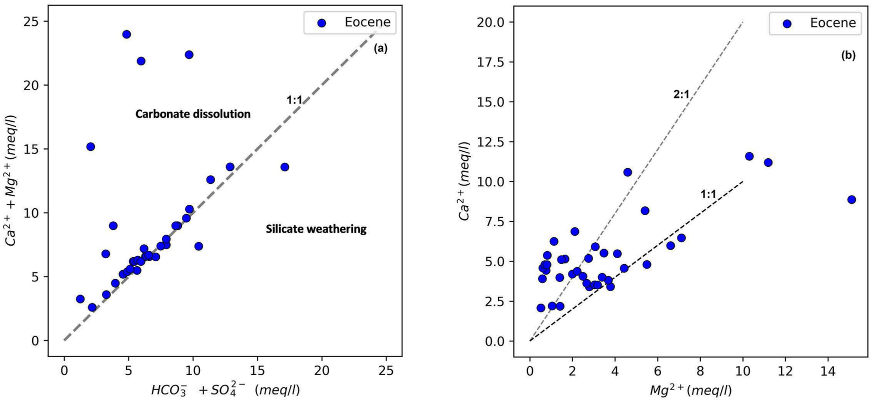

Figure 5. Scatter plot of (a) $Ca^{2+} + Mg^{2+}$ versus $SO_4^{2-} + HCO_3^-$ and (b) Ca^{2+} versus Mg^{2+}

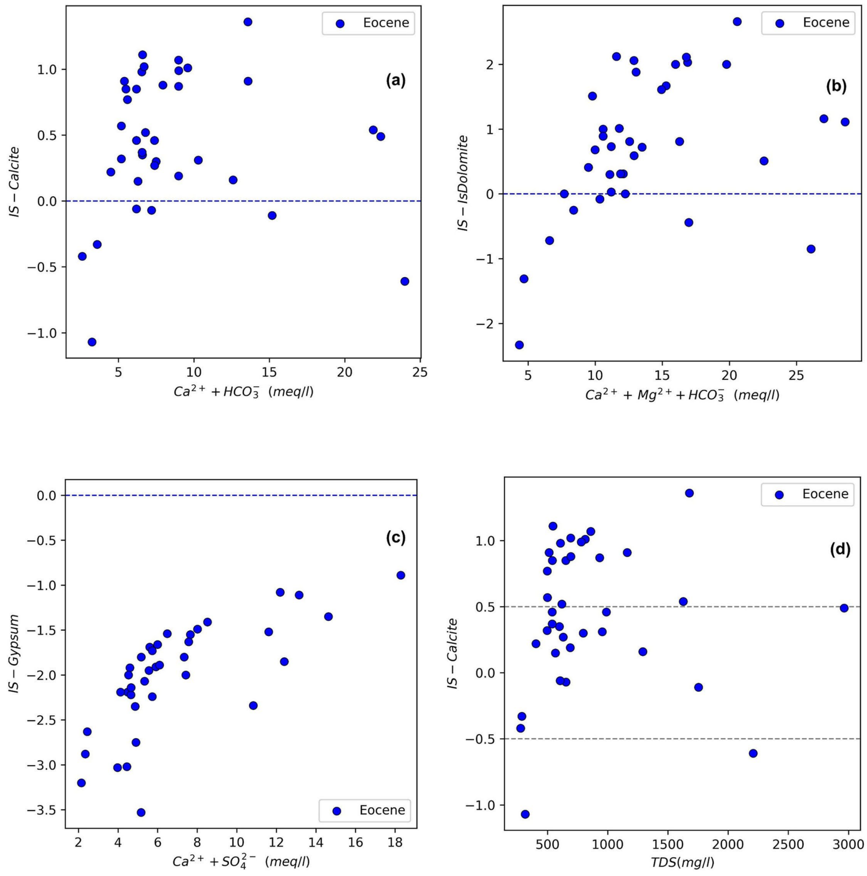

Figure 6. Scatter plot of Saturation index (a) Calcite, (b) Dolomite, (c) Gypsum and (d) Saturation index of Calcite vs TDS.

In a groundwater system, the ion exchange process is a significant factor that plays a very important role in the evolution of groundwater chemistry. This exchange process, which takes place between water and aquifer materials, generally occurs during the groundwater flow or during its storage. To ascertain whether the variation in the chemical composition of groundwater in the area is related to the influence of the ion exchange process, we have established the relation Ca^{2+} +

$Mg^{2+} - SO_4^{2-} - HCO_3^-$ as a function of $(Na^+ + K^+) - Cl^-$. This relationship only allows us to highlight these basic exchange processes, since other processes that may contribute to the input of solutes, such as the dissolution of minerals and marine intrusion, are not taken into account (Faye, 2005). If the cation exchange process is a significant groundwater composition controlling process, the relation between these two parameters should be linear with a slope of −1 (Fisher & Mullican III, 1997; Rajmohan & Elango, 2003). In the current study, the plot of $Ca^{2+} + Mg^{2+} - SO_4^{2-} - HCO_3^-$ versus $(Na^+ + K^+) - Cl^-$ shows a strong correlation between the two parameters. Groundwater samples point fall along or close to a straight line ($r^2 = 0.88$) with a slope of −0.97 which is very close to −1 indicating that ion exchange is an important hydrochemical process influencing groundwater quality in the study area (**Figure 7(a)**). However, a few groundwater samples fell above and below the linear trend line indicating that the chemical composition of groundwater is not controlled only by ion exchange process. Furthermore, the influence of ionic exchange on the variation of groundwater chemistry can be verified by plotting the data on bivariate plot of $(Ca^{2+} + Mg^{2+})$ versus $(HCO_3^- + SO_4^{2-})$ (**Figure 5(a)**). Ion exchange tends to shift the plotted points towards the right due to a large excess of $(HCO_3^- + SO_4^{2-})$ and towards the left in case of reverse ion exchange and dominance of $(Ca^{2+} + Mg^{2+})$ over $(HCO_3^- + SO_4^{2-})$ (Cerling et al., 1989; Fisher & Mullican III, 1997; Kumar et al., 2006; Srinivasamoorthy et al., 2008).

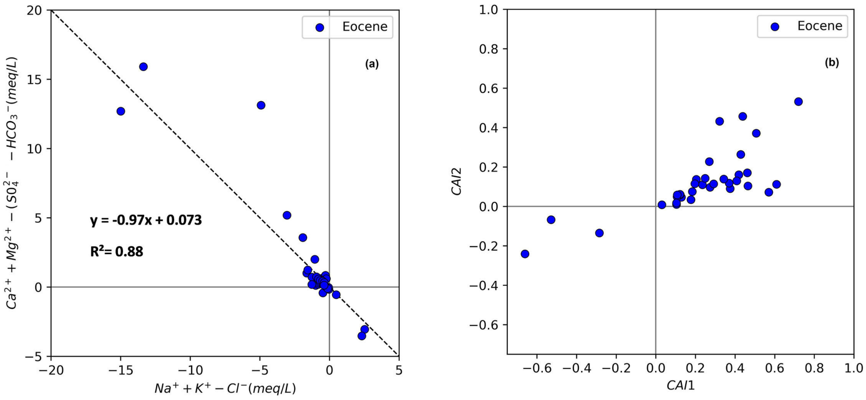

Figure 7. Scatter plot of (a) $Ca^{2+} + Mg^{2+} - SO_4^{2-} - HCO_3^-$ versus $(Na^+ + K^+) - Cl^-$; (b) CAI-2 versus CAI-1.

Another significant way to check the importance of ion exchange in hydrogeological system is to calculate the Chloro-alkaline index (CAI). The chloro-alkaline indices CAI-1 and CAI-2 proposed by Schoeller (1977) are widely used by several researchers (Kumar et al., 2007; Li et al., 2013; Singh et al., 2012; Zaidi et al., 2015; Zhang et al., 2022) to characterize the influence of the ion exchange process on the evolution of groundwater chemistry. These indices are computed using the following Equation (2) and Equation (3):

$$\text{CAI-1} = Cl^- - (Na^+ + K^+)/Cl^- \quad (2)$$

$$\text{CAI-2} = \text{Cl}^- - \left(\text{Na}^+ + \text{K}^+\right) / \text{SO}_4^{2-} + \text{HCO}_3^- + \text{CO}_4^{2-} + \text{NO}_3^- \tag{3}$$

where all ions are expressed in meq/L.

If there is an ion exchange between Na^+ and K^+ in the groundwater with Ca^{2+} and Mg^{2+} in the aquifer material, both the above indices will be positive indicating reverse ion exchange and the exchange is known as direct. On the other hand, when there is an ion exchange between Ca^{2+} and Mg^{2+} in groundwater with Na^+ and K^+ in the rock, the exchange is known as indirect, and the above indices will be negative, indicating ion exchange (Ntanganedzeni et al., 2018; Zaidi et al., 2015). Negative value of CAI indicates chloro-alkaline disequilibrium, and the reaction is also known as the cation-anion exchange reaction (Marghade et al., 2012; Singh et al., 2013). The computed values of CAI in the study area reveal that the majority of groundwater samples (91.9%) have positive CAI values indicating the predominance of reverse ion exchange process occurring in the study area due to direct exchange of Ca^{2+} and Mg^{2+} from the aquifer matrix with Na^+ and K^+ from the groundwater (**Figure 7(b)**). Indeed, reverse exchange phenomena are caused by the carbonate nature of aquifers, but also saline intrusion phenomena. In fact, when seawater mixing freshwater in aquifer, cation exchange occurs and sodium is absorbed by the exchanger (clay), and calcium is released (Faye et al., 2003). In fact, the frequency of tectonic events during the Eocene led to seawater getting trapped in certain parts of the upper aquifer, causing it to mix with freshwater. In the remaining groundwater samples, representing 8.1%, the values of CAI are negative indicating the occurrence of cation-anion exchange process in which Ca^{2+} and Mg^{2+} in groundwater are exchanged with Na^+ and K^+ of aquifer material. This occurs through the mechanism of cation exchange on clay minerals. Further the plot of (Ca^{2+} Mg^{2+}) versus ($Na^+ + K^+$) shows that, except one groundwater sample, all the other groundwater samples fall above the 1:1 trend line indicating the dominance of alkaline earths ($Ca^{2+} + Mg^{2+}$) over alkaline ($Na^+ + K^+$) in groundwater then confirming the reverse ion exchange process (**Figure 8**).

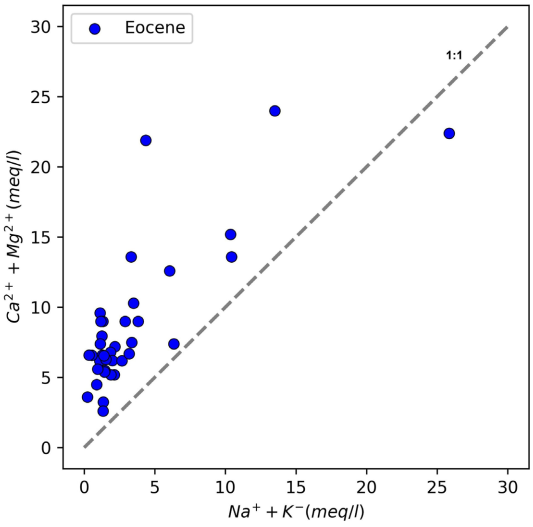

Figure 8. Scatter plot of $Ca^{2+} + Mg^{2+}$ versus $Na^+ + K^+$.

It is important to remember that evaporation is a very important process in arid and semi-arid areas. It influences the variation of groundwater chemical composition. particularly in shallow aquifers. In general, it is expected that the evaporation process would cause an increase in concentrations of all species in water. If the evaporation process is dominant, assuming that no mineral species are precipitated, the Na/Cl ratio would be unchanged (Jankowski & Acworth, 1997). Additionally, the Na^+/Cl^- ratio is usually applied to determine the salinity and saline intrusion mechanisms in semi-arid regions (Nematollahi et al., 2016). Furthermore, weathering of silicate rock minerals, and halite are generally considered as the main processes controlling the high content of Na^+ in groundwater. If the concentration of Na^+ is mainly derived from halite dissolution, the Na^+/Cl^- ratio should be approximately equal to 1, whereas a ratio greater than 1 is typically interpreted as Na released from the weathering of silicate minerals (Barzegar et al., 2016; Meybeck, 1987). In this study, the Na^+/Cl^- ratio of groundwater samples ranged from 0.23 to 1.61 with an average of 0.70. The majority of groundwater samples have a Na^+/Cl^- ratio less than 1, suggesting reverse ion exchange is the dominant process in the study area. **Figure 9** shows that most of the groundwater samples lie below of the sea water ratio (0.86) equiline, indicating the dominance of Cl^- over Na^+ confirming marine influence (Diedhiou et al., 2012).

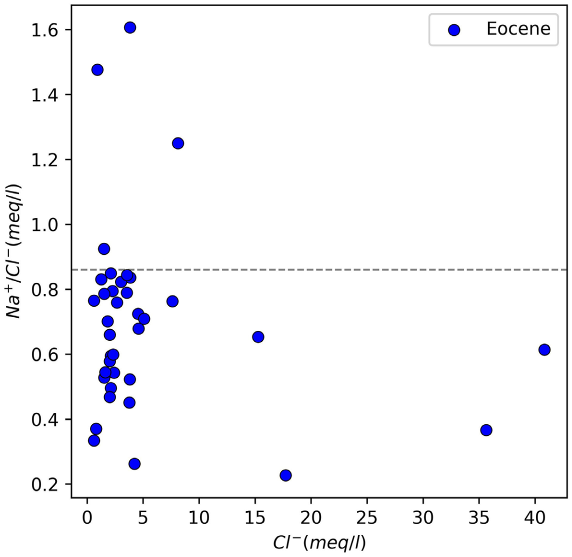

Figure 9. Scatter plot of Na^+/Cl^- versus Cl^-.

5. Conclusion

Groundwater of the Eocene aquifer has been investigated, using various hydrogeochemical approaches: geochemical plots, binary diagram, and ionic ratios in order to assess its quality and especially to determine the main hydrogeochemical processes controlling groundwater quality. In the majority of groundwater samples, the analyzed chemical parameter such as Ca^{2+}. Na^+, K^+, Cl^-, SO_4^{2-} , and

NO_3^- are well within the permissible limits for drinking water suggesting the suitability of groundwater for drinking purposes. Fluoride content of groundwater samples compared with the permissible limit for drinking water purposes by the WHO indicates that all groundwater samples are suitable for drinking purposes. Several water types are shown in the piper diagram, of which Ca^{2+}- HCO_3^- constitutes the dominant facies in groundwater. The water-rock interaction is the factor controlling the chemical composition of water. This is confirmed by the study of ionic ratios which show that calcium and magnesium come from the dissolution/precipitation of carbonate minerals and reverse ion exchange process. The statistics approach and computed values of CAI indicates that the majority of groundwater samples (91.9%) indicate the predominance of the reverse ion exchange process occurring in the study area due to direct exchange of Ca^{2+} and Mg^{2+} from the aquifer matrix with Na^+ and K^+ from the groundwater and confirming mixing seawater and fresh water. This study allows a better knowledge of the processes responsible for the mineralization of groundwater, largely exploited by populations, for better management of the resource by decision-makers. Indeed, the most productive aquifer in the area (Maestrichtian) has brackish waters that limit all socio-economic activities.

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Ethics Approval and Consent to Participate

The study involving human participants was reviewed and approved by all authors from Cheikh Anta Diop University in Dakar.

Availability of Data and Matériel

Data will be made available on request.

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Author Contributions

Mouhamet Moustapha Diaw: Conceptualization, Review and editing, Writing-original, Data curation, Investigation, Formal analysis validation; Mathias Diedhiou: Conceptualization, Data curation, Data processing, Formal analysis, Writing-original draft, Review, Editing, Validation. Ousmane Coly Diouf: Data processing, Writing-review & editing, validation. Moctar Diaw: Conceptualization, Writing-review & editing. Serigne Faye: Supervision, conceptualization, Writing-review & editing, validation.

Conflicts of Interest

The authors declare that they have no conflict of interest.

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