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Rock-Water Interactions and its Hydrogeochemical processes of Groundwater Resources: A Case Study for Mandya District of Karnataka State, India

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***Abstract*:** Rock-Water interactions and hydrogeochemical processes are critical for understanding groundwater chemistry and the environmental impacts of various geological formations. These interactions involve several chemical processes that significantly influence the composition and groundwater quality. The present study aims to investigate the rock-water interactions and hydrogeochemical processes through the water samples collected from Mandya district. The study involved Piper's diagram, Gibb's diagram and Scatter plots of various parameters in revealing chemical processes that influence hydro geochemistry. The concentrations of these ions varied spatially and temporally in different taluks of Mandya district, depending on the lithological formations of those locations. Ions were dominated by Na>Ca>Mg>K = HCO_3>Cl>SO_4>CO_3. Ca-Mg-Cl, Ca-Na-HCO_3, and Ca-HCO_3 types were the dominant hydro chemical facies noticed in the study area. Hydrogeochemical processes provide valuable insights into the complex systems of rock-water interaction and to aid in effective groundwater management and pollution mitigations.

***Keywords*:** Rock-Water Interactions, Hydrogeochemical processes, Mandya

Groundwater contributes to about eighty percent of the drinking water requirements in the rural areas, fifty percent of the urban water requirements and more than fifty percent of the irrigation requirements of the nation (CGWB 2012). Rock-water interaction is the complex chemical and physical processes that occur when groundwater interacts with geological materials. Rainwater enters the ground's surface, penetrates it, and runs through the soil and rock zones (Yousif and Aassar 2018). Several chemical reactions occur during groundwater migration, depending on the chemical makeup of the water, the rock in its flow path, and the amount of time spent in residence (Yousif and Aassar 2018). This interaction is crucial in hydrogeology, as it alters the chemical composition of groundwater, which is influenced by the minerals present in the rocks (Yousif and Aassar 2018). Minerals within rocks can dissolve in water, releasing ions into the groundwater and even precipitate out of solution, forming new minerals (Ye et al., 2024). This process involves the exchange of ions between the water and the mineral surfaces, affecting the concentration of various chemical species in the groundwater (Rajmohan and Elango 2003). Oxidation and reduction reactions can alter the mobility of certain elements, particularly metals, influencing groundwater quality and contaminant transport (Basavarajappa et al., 2015c).

The mineral composition of hard to soft rocks (igneous, sedimentary, or metamorphic) affects how easily they interact with water. Limestone (sedimentary) is more susceptible to dissolution than granite (igneous). The initial chemical composition of the groundwater plays a critical role in determining the extent and nature of rock-water interactions (Elango and Kannan 2007). Groundwater can be classified into various types based on its chemical constituents, such as Ca-HCO_3, Na-Cl, and Ca-SO_4, which reflect the dominant rock-water interactions occurring in each area. Factors like temperature, pressure, and the presence of organic materials can influence the rates and types of chemical reactions that occur during rock-water interactions (Rasool and Ahmad 2023). Rock-Water interaction and hydrogeochemical processes are key to determining the quality of groundwater resources, which are vital for drinking water, agriculture and industrial suitability. Knowledge of these processes helps in assessing the impacts of human activities, such as mining and agriculture, on groundwater systems and in developing strategies for pollution mitigations (Li et al., 2021). Insights into rock-water interactions are crucial for the exploration and management of natural resources, including minerals and hydrocarbons.

MATERIAL AND METHODS

Site description: Mandya district is in the south-eastern part of Karnataka State with geographical area of 4,850 km^2 and situated between 12^{0}13' to 13^{0}04' latitude and 76^{0}19' to 77^{0}20' longitude (Fig. 1) (Sagar et al., 2024). It comprises seven taluks namely Krishnarajpet, Maddur, Malavalli, Mandya, Nagamangala, Pandavapura, and Srirangapatna with elevations ranged from 600 to 1045 mts above mean sea level (Sagar et al., 2024). The district forms the part of the southern maiden area, which comprises of broad undulating plateau and slopes towards the southeast. It enjoys tropical to sub-tropical climate with temperatures ranging from 16^0 to 37^0C with an average annual rainfall of 750 mm. The hottest month is April, and the temperature drops significantly as the southwest monsoon arrives in June and reaches coldest during December. The district falls under the rain shadow zone of Western Ghats and receives most of its rainfall during monsoon seasons (Thimme Gowda et al., 2015). Most of the district is covered by red sandy soil, followed by red clay soil, medium black soil and lateritic soil.

Agriculture and irrigation: Cauvery is the major river flowing towards east direction along with its tributaries namely, Hemavathi, Shimsha, Lokapavani and Veeravaishnavi (Begum and Harikrishnarai, 2008). Apart from these rivers, the district is endowed with number of streams, which along with the rivers form sub dendritic drainage patterns. The Krishnaraja Sagara reservoir was built for the Cauvery River, which is the primary source of water for irrigation in much of Maddur, Mandya, Srirangapattana, Pandavapura, and Mallavalli taluks (CGWB 2012). It is predominantly an agricultural district, benefitting from irrigation from the River Cauvery for the major crops of paddy, ragi, jowar, maize, pulses, oil seeds, sugarcane, cotton, fruits and various vegetables (CGWB 2012). K.R pete, Nagamangala and some sections of Mandya and Mallavalli taluks are dry areas and rely on groundwater for irrigation. Mandya is one of the most fertile districts of the state, and various surface and groundwater plays an important role in irrigating (CGWB 2012).

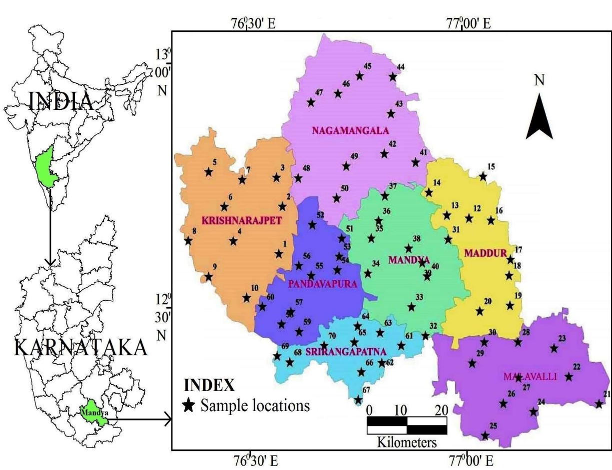

Fig. 1. Groundwater samples location map of Mandya district

Geological settings: The study area falls under Western Dharwar Craton and Peninsular Gneiss and comprises 3.4-3.0 Ga ancient 'Supracrustals' (Sargur Group) and tonalite-trondhjemite-granodiorite (TTG) basement overlain unconformably by 2.9-2.6 Ga greenstone belts (Radhakrishna and Vaidyanathan 1997). Gneiss, granite, pegmatite, and ultramafic rock & dykes are the major rock types observed during limited field visits (Fig. 2a) (Sarbajna et al., 2018). Gneiss, granite, amphibolite schist, and excess mica mineral are identified near Melukote area (Babitha Rani et al., 2015). The Peninsular Gneisses cover almost 80% of the areal extent of Mandya district (Suresha 2016). Small patches of porphyritic granite of Closepet age are also exposed (Sukanta Dey et al., 2003). From the groundwater point of view, these rocks are classified as crystalline formations (Baiocchi et al., 2016). The fracture/fissure system formed along with joints and faults traversing the rocks facilitates groundwater circulation and hols a moderate amount of water (Basavarajappa et al., 2015b). Groundwater quality is determined by the mineralogical composition of the rocks. Conglomerate, amphibolite, pelitic schist, quartzite, iron formation, small carbonate bodies, and volcanic rocks from the Nagamangala schist belt were also encountered. In the metasediments, bedding planes and the fractures facilitate water movement and accumulation (CGWB 2012). The schistose rocks are poor aquifers and yield water of poorer quality in very less quantity. Groundwater generally occurs in the water table conditions in the weathered and decomposed mantle and under semi-confined conditions in the deeper fractures (CGWB, 2012). There are few sporadic outcrops of rocks where Cauvery River breaks through the hills ranges with waterfall and few fertile shallow valleys.

Data collection & analysis: The methodology for water samples collection was designed to ensure that the samples accurately reflect the groundwater chemistry and the interactions occurring with surrounding rocks. 70 groundwater samples were collected at random on geological features, proximity to potential contamination sources, areas with known mineral deposits and hydrological characteristics (Sagar et al., 2024). Groundwater was collected in sterile, clean polyethylene sampling bottles to determine the concentration of water quality parameters using WHO and BIS (Basavarajappa et al., 2015a). The same day, the bottles were washed with distilled water and rinsed with the same water samples and sent to the laboratory (Sagar et al., 2024). The groundwater was filled up to about 80% of bottle capacity to allow for expansion and prevented overflow. Garmin GPS etrex-10 portable equipment was utilized in recording each sample locations precisely within the district during the Pre-monsoon period (April) of the year 2023 (Fig. 1) (Manjunatha and Basavarajappa 2015). The bottles were stored in a cooler with ice packs during transportation to the laboratory to maintain temperature and prevent changes in water chemistry, since these were collected during summer season of 2023 (Sagar et al., 2024).

Samples were treated with nitric acid for cation analysis and kept at 4^{0}C for anion analysis. The present analysed parameters include electrical conductivity (EC), potential of hydrogen (pH), and cation groups like calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), and anions groups like bicarbonate (HCO_3), carbonate (CO_3^{2-}), sulphate (SO_4^{2-}), and chloride (Cl^-) (Sagar et al, 2024). EC, pH, and TDS were estimated in the field by using a Hanna field meter; Ca^{2+}, Mg^{2+}, and Cl^- were measured using a volumetric titration method; Na^+ and K^+ were determined using a Flame Photometer; F- was estimated using a visual interpretation technique; and SO_4^{2-} was recorded using a turbidity method in accordance with BIS Standard (Ramesh and Elango 2012). Scatter plots for geochemical modelling was performed using Sigma plot software in understanding the processes of rock-water interactions and predicting groundwater behaviour (André et al., 2005).

RESULTS AND DISCUSSION

Hydrochemistry: EC concentration ranged from 291 to 2472 μS/cm, while the pH ranged from 6.7 to 8. Ion's dominance in the district followed the order of Na> Ca> Mg>K = HCO_3>Cl>SO_4>CO_3 (Table 1). The concentration of major anions and cations were observed in the collected water samples through Piper's diagram (Fig. 2b) (Sircar et al., 2022). Another most used graphical technique that is crucial for the reduction of chemical data is the Piper trilinear diagram (1994). It consists of a diamond-shaped quadrilateral situated between two neighbouring equilateral triangles. Ca-Mg-Cl, Ca-Na-HCO_3, and Ca-HCO_3 were the three hydrogeochemical facies types of Groundwater noticed in Mandya district. Ca-HCO_3 (calcium-carbonate) is the superior form of water among the collected samples, indicating that the above water type is the result of groundwater replenishment and agricultural water return flow. The chemical composition of groundwater is determined by the interaction of rock and water (Jiang, et al., 2023).

Major Ion Chemistry and Chemical Processes

Calcium and magnesium: Calcium is the second most dominant cation noticed among the collected water samples that ranged from 14.4mg/l to 144mg/l. Calcium, sodium, and magnesium are associated with minerals such as

Table 1. Minimum and maximum values of major ion concentration

Unit	Milligram per Litre (mg/l)								EC(μS/cm)
Parameters	Ca	Mg	Na	K	CO_3	HCO_3	Cl	SO_4	
Minimum	14.4	6.4	21.95	0.28	0.1	94.9	13	2.98	291
Maximum	144	111.6	276.65	78.95	5.49	900.3	254	251	2472

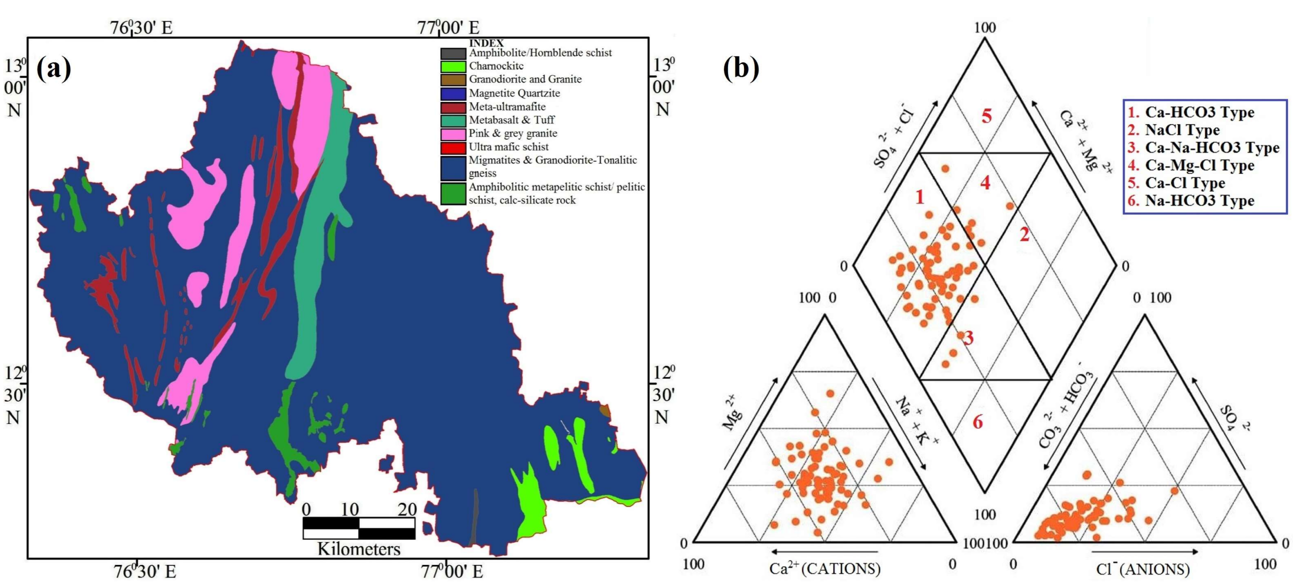

Fig. 2(a). Lithology map of Mandya district; **(b)** Piper's diagram showing hydrogeochemical facies montmorillonite, aragonite, illite, and chlorite (Basavarajappa et al., 2015c). The calcium content of the groundwater is due to the dissolution of $CaCO_3$ and $CaMg\ (CO_3)_2$ precipitates during recharge (Lakshmanan et al., 2003). (HCO_3+SO_4) vs (Ca+Mg) scatter plot reveals that silicate weathering causes ion concentration to decrease below equiline (Fig. 3c). Carbonate weathering is responsible for the concentration exceeding the equiline. The concentration drops along the equiline was caused by both silicate and carbonate weathering (Batabyal and Gupta 2017). (HCO_3+SO_4) vs (Ca+Mg) scatter diagram (Fig. 3c) of the study area indicated that most of the dots are along the equiline, with a few below and above it. This suggests that both silicate and carbonate weathering occur, with silicate weathering being more prevalent than carbonate weathering (Xiong et al., 2022). In the scenario, rainwater combines with atmospheric carbon dioxide to generate carbonic acid, which then reacts with calcium carbonate in the soil to form bicarbonate and calcium ions (Batool et al., 2024). Magnesium concentrations ranged is 6.4 to 111.6 mg/l.

Sodium and potassium: Sodium is the predominant cation in the study area that ranged from 13.69 to 5.15 mg/l. The 1:1 ratio between Na and Cl implies halite breakdown and increased Na concertation, with Cl interpreted as Na released from silicate weathering (Fig. 3a & 3b) (Mayback, 1998; Deutsch 1997). The concentrations of some samples falling below the 1:1 line of the Na vs Cl scatter diagram revealed silicate weathering, whereas concentrations above the 1:1 line of the Na vs Cl scatter diagram (Fig. 3d) shows no halite dissolution occurs. Increased concertation HCO_3 compared to Na concertation in groundwater indicated silicate weathering. Na vs HCO_3 scatter plot (Fig. 4b) showed HCO_3 concentration is high than Na, indicating silicate weathering. This implies that ion exchange mechanism diminished the Na concentration in groundwater and the same process was also supported by Na vs Ca scatter plot (Fig. 3e). The Na+K vs Total Cation scatter plot was evaluated the cation input to groundwater due to silicate

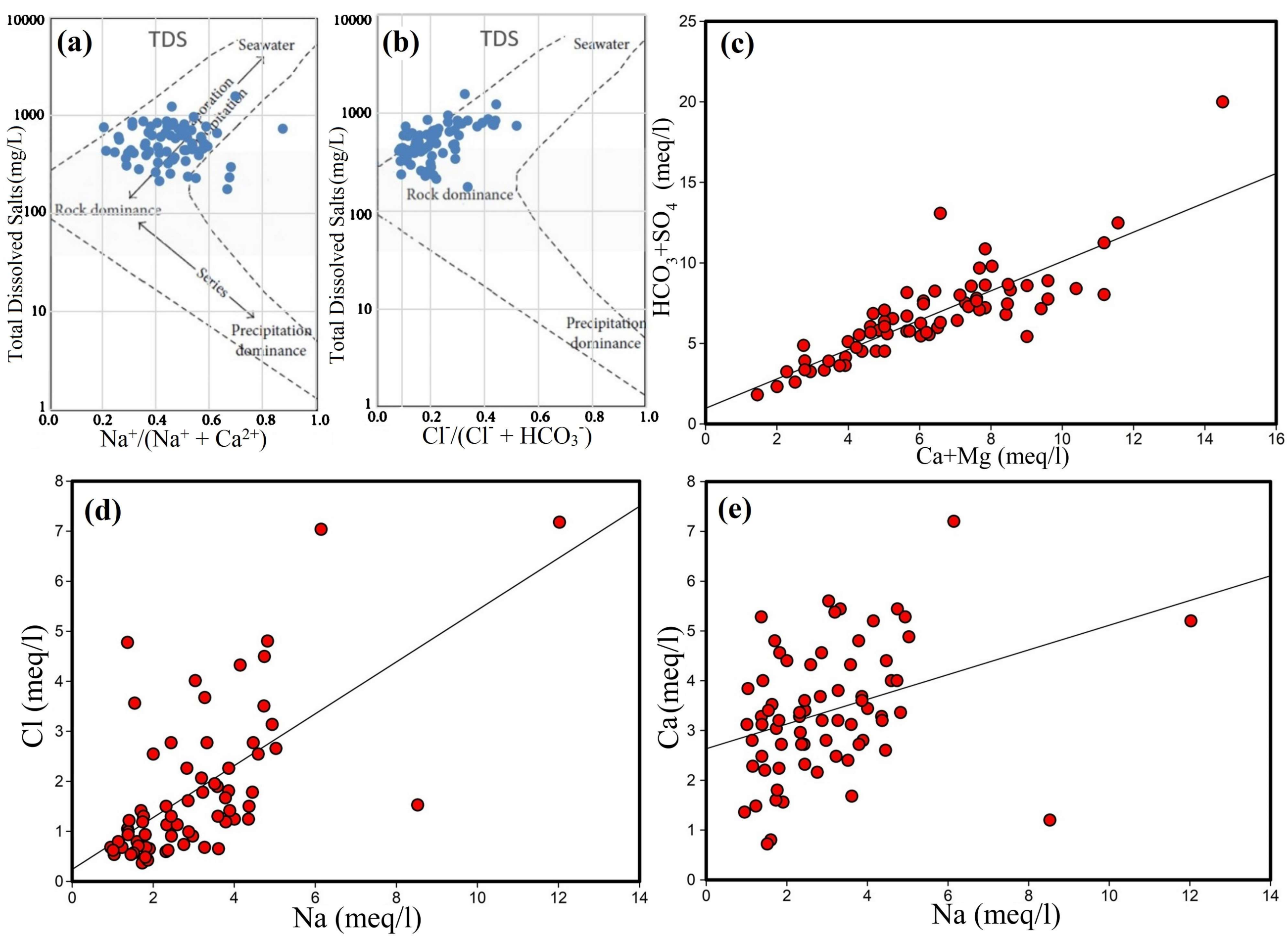

Fig. 3 (a. b) Gibb's Diagram showed the Rock-Water interactions and Scatter plots of © Ca+Mg vsHCO_3+ SO_4; **(d)** Na vs Cl; **(e)** Na vs Ca weathering. The Na+K vs Total Cation scatter map (Fig.4a) highlighted the points both above and below equiline that show cation in groundwater caused by silicate weathering. Potassium concentrations ranged from 0.28 to 73.91 mg/l.

Chloride, bicarbonate and sulphate: Bicarbonates was the predominant anion and ranged from 94.9 to 900.3 mg/l. When rainfall occurs, it combines with atmospheric carbon-dioxide to generate carbonic acid, which enters the earth and dissolves carbonate minerals. During recharge, HCO_3 and Ca will be released into groundwater. The Na vs HCO_3 concentration scatter plot (Fig. 4b) illustrated the silicate weathering increased the HCO_3 concentration in groundwater. Chloride concentrations observed to be derived from rainwater and ranged from 13 to 254 mg/l. Evaporation increased the chloride concentration in groundwater, as showed by the EC vs Na/cl scatter plot (Fig. 4c). The concentration of sulphate ranged from 6 to 251 mg/l. There is no acid rain noticed in Mandya, hence the sulphate formed via gypsum dissolving. The concentration of SO_4 vs Cl scatter diagram (Fig. 4d) revealed a low concentration of sulphate, indicating that sulphate is being depleted through sulphate reduction. As a result, sulphate concentrations in groundwater were low due to sulphate reduction or a lack of a source (Miao et al., 2012).

The main industries at Mandya are sugar mill, sugar units, jiggery producing units, rice, oil and solvent extract units (Solomon 2011). The sugar factory is one of the biggest in the nation. Chemical and Paper mill at Belagola near to Mandya town, Milk dairy at Gejjalagere, BPL battery factory and several small-scale industries were also noticed. Other major industry includes garments, textiles and engineering based. The rural population of Mandya district constituted more than 80% who involved in the vast agricultural and irrigational activities (CGWB 2012). Both industrial and agricultural activities had attributed to more use of fertilizers, pesticides, chemicals in canal irrigation.

The groundwater chemistry was influenced by the geology of the water-bearing formations of Dharwar Schist

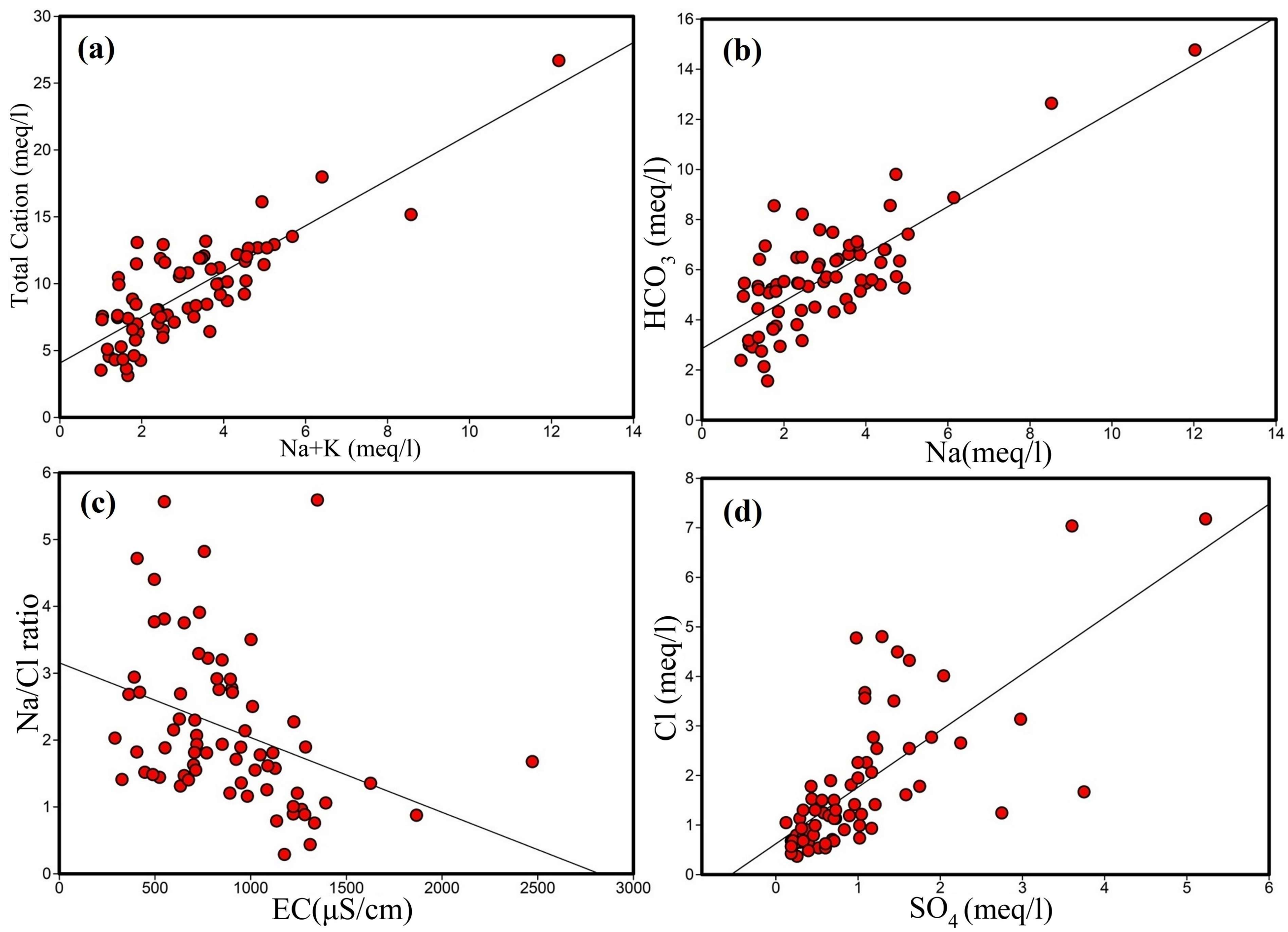

Fig. 4. Scatter plots for **(a)** Na+K vs Total cation; **(b)** Na vs HCO_3; **(c)** EC vs Na/Cl indicated Evaporation; **(d)** SO_4 vs Cl showed Sulphate reduction

and peninsular gneisses/ granites (Prasanna Kumar and Nagaraju 2000). Mandya groundwater was supersaturated with minerals like gibbsite, goethite, hematite, aragonite, calcite, dolomite, and alunite due to rock-water interactions (Yousif and El-Aassar 2018). Geoelectrical and hydrochemical studies reveal that the ions in the groundwater mostly originate from rock-water interaction, with a few samples showing precipitation dominance (Sandeep et al., 2023).

The dissolution of minerals like $CaCO_3$ and weathering of rocks were the main sources for major and trace elements leading to higher concentrations of ions like sodium, calcium, magnesium, and potassium (Yousif and El-Aassar 2018). Higher total dissolved solids (TDS) in the groundwater were attributed to the longer residence time of water in the subsurface and rock-water interaction processes (Prasanna Kumar and Nagaraju 2000). High chloride concentrations were observed in eastern part of Mandya and around Maddur. Gibbs plots indicate that groundwater samples in both seasons in Mandya has an interaction between the lithological units and the percolating water into the subsurface (Shivashankara et al., 2016).

CONCLUSION

Mandya is in Precambrian hard rock terrains with extended rock-water interaction and serve as the primary source of groundwater chemistry. Bicarbonates, calcium, and sodium were the dominant ions recorded in the collected water samples. The study region revealed three dominant hydrogeochemical faces such as Ca-Mg-Cl, Ca-Na-HCO_3, and Ca-HCO_3. This includes calcium-carbonate dissolution, silicate weathering, and ion exchange. These processes regulate groundwater chemistry contributed to a better understanding of the hydrogeochemical properties of Mandya aquifers. The rock-water interactions, aquifer geology, mineral dissolution, weathering, and seasonal recharge patterns were the key factors influencing the groundwater chemistry and quality in Mandya region. Continuous monitoring and management of these processes is important for sustainable groundwater use in the region.

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