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RESEARCH ARTICLE - HYDROLOGY AND HYDRAULICS

A multivariate statistical approach to evaluate the hydro-geochemistry of groundwater quality in the middle Ganga river basin, Patna, India

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Abstract

The study of groundwater samples from Patna, which is in the middle Ganga River basin in the state of Bihar, was done to evaluate the hydrogeochemical nature of groundwater and figure out the controlling factors that affect its ionic chemistry. This study's groundwater samples were taken seasonally from 20 Patna, Bihar locations from 2019 to 2020 and analyzed for their physical and chemical properties using APHA's standard methods. Multivariate statistical techniques, such as Correlation matrix, Principal Component Analysis and Hierarchical cluster analysis, were carried out on the analytical variables, followed by interpreting the groundwater's geochemical nature using Durov Plot, Piper plot, ion-scatter plots and Gibb's diagram. The results obtained were compared with water quality standards prescribed by the Bureau of Indian Standards. The study revealed that groundwater's alkaline nature and water's total hardness varied from hard to very hard categories. Total dissolved solids range from 158 to 575 mg/l, where 31.66% of samples have exceeded the desirable TDS limit for drinking water. The abundance of anions was observed in decreasing order ($HCO_3^- > Cl^- > SO_4^{2-}$) during all seasons and cations as $Ca^{2+} > Na^+ > Mg^{2+} > K^+$ in pre-monsoon and post-monsoon, whereas in monsoon season, it was observed as $Mg^{2+} > Na^+ > Ca^{2+} > K^+$. Ca^{2+}–Mg^{2+}–HCO_3^- type water was revealed as the significant hydrogeochemical facie, and the reverse ion exchange process was observed to be the governing factor in 77% of the total groundwater samples. Gibbs's diagram showed rock–water dominance as a major factor in groundwater ionic composition during all seasons.

Keywords Groundwater · Durov plot · Piper plot · Scatter plot · Hydro-geochemistry

Introduction

Groundwater is the most important natural resource of fresh water and is critical for living organisms' survival (Hui et al. 2020; Sharma and Sharma 2022; Olatunde et al. 2022). Globally about 2.5 billion people depend on it for domestic, agricultural, and industrial purposes (Khan and Jhariya 2017; Gao et al. 2020; Nizam et al. 2022). Several researchers reported that Groundwater quality is deteriorating with the passing decades due to rapid industrialization, increasing population, overexploitation, excessive use of fertilizers and pesticides in intensive agriculture practices, and mixing of untreated municipal and industrial effluents (Liu et al. 2019; Bulut et al. 2020; Kom et al. 2022; Makubura et al. 2022). Besides these, groundwater chemistry is also influenced by the change in lithological characteristics, climatic conditions, general geology, rock–water interaction, quality of recharge water, time of retention of water in the hosted aquifer, and the flow directions of water under the ground (Varol and Davraz 2015; Ahmed and Clark 2016; Eang et al. 2018; Sulaiman et al. 2023; Tiwari et al. 2017). Groundwater in arid and semi-arid regions is more vulnerable to contamination because of changes in the aquifer's mineral weathering process and uneven resource distribution (Hui et al. 2020). Patna, the state capital and the most populated city of Bihar, is experiencing continuous deterioration in groundwater quality.

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According to data from the Master plan of Patna (2016), water supply within Patna urban area is from 85 deep tube wells dug in different parts of the city and from deep aquifer pumping by private households. Though, poor and old water supply networks, poor sanitation, improper effluent disposal facilities, and poor sewerage system within Patna pose potential threats to the quality of groundwater reserves. Therefore, knowledge of the study area's groundwater chemistry can be necessary for determining its use for various purposes. However, extensive groundwater quality assessment becomes difficult as the water quality depends on numerous physicochemical parameters and other controlling factors. Thus, assessing groundwater quality with hydro-geochemical properties over space and time can be a vital tool for solving problems and planning a proper management strategy for groundwater, as it will help us to figure out the mechanism of interaction between groundwater and the environment (Panigrahy et al. 1996; Atwia et al. 1997; Ballukraya and Ravi 1999; Ramappa and Suresh 2000). Different graphical techniques (e.g., Piper, Durov) and bivariate ion scatter plots have been developed to visually understand hydrogeochemical data to show water classification, sources of water solutes, dissimilarities of water composition and quality (Gaikwad et al. 2020). Multivariate statistical analysis and analytical procedures such as principal component analysis (PCA) and hierarchical cluster analysis were also utilized to comprehend and explain the complicated water quality system. Several researchers have agreed with the advantages of using these techniques in concise, large, complex sets of analytical data to relatively simple interpretable numbers (Maliqi et al. 2020; Kadam et al. 2021; Kumar et al. 2023). Singh et al. (2009) reported the fitness of PCA and HCA in water quality assessment, evaluation of the current ecological status of the aquifer system, and identification of the potential source of contamination in the groundwater. Although several researchers have conducted studies on groundwater quality in various districts of the Middle Gangetic Plains, India (Srinivasamoorthy et al. 2011; Prasanna et al. 2011; Kumar et al. 2018; Singh et al. 2015; Shukla and Saxena 2020; Maurya et al. 2020), and in Patna (Rai et al. 2011; Sinha et al. 2011; Sukumaran et al. 2015; Zafar et al. 2022), the literature review revealed that little work had been done on the hydro-geochemical characterization of groundwater of Patna. Hence, the study attempts to identify hydrogeochemical processes in groundwater in Patna to examine the dominant factors responsible for determining the chemical composition of groundwater. The results of this study will contribute to improving the understanding of the factors controlling groundwater quality in Patna, will provide a baseline study in this direction for the study area, and can also help identify suitable water sources for the intended use and proper use management of groundwater resources.

Study area

The study was conducted in Patna, India's capital and largest city, Bihar. Patna is situated in the middle Ganga River basin on the northern edge of the south bank of River Ganga, 47 m above mean sea level between latitude 25°13' N–25°45' N and longitude 84°43' E–86°44' E, covering an area of 3172 Km^2 (Fig. 1). The study area has a monotonous flat topography. It is laid down by the alluvial sediments of River Ganga and northerly flowing streams of the Pre-cambrian period, deposited unconformably on the Archaean basement (Sandhu et al. 2011; USGS 2022). The majority of land in Patna is under residential usage (47.5%) (Patna Master Plan 2031 2016). Agriculture (17.66%), public and semi-public (10.18%), transportation (5.90%), and commercial use (4.46%) are some of the other contributors (Zafar et al. 2022). According to the Census of India (2011), the population of Patna is 2,049,156, of which 1,087,285 are males and 961,871 are females. Groundwater aquifer of the Middle Gangetic Plain is characterized as unconfined or semi-confined sandy sediments that move through the joints, fissures, and other associated rocks of the Pre-Cambrian age like granites gneisses, mica-schist and quartzite (CGWB 2013; Kumar et al. 2019a). The climate is subtropical and is characterized by hot summers with an average temperature of 32.4 °C and relatively cold winters with an average temperature of 17.2 °C. The average annual rainfall is 1076 mm, with substantial rain falling in July and August. Relative humidity can reach 100% during summer (Sulaiman et al. 2021). River Ganga drains the city in the north, Sone in the west, and the central part of the city is drained by Punpun, Phalgu and their tributaries (CGWB 2013).

Materials and methods

Water sample collection and chemical analysis

The study adopted a systematic random sampling method to collect groundwater samples at a regular interval of ~3 km from one site to another. Groundwater samples were collected seasonally in pre-monsoon with the onset of the summer season (March–April), near the end of the monsoon (August–September) and in the post-monsoon month of October–November. The samples were collected from 250 to 300 ft. deep boreholes located at 20 different sites in the study area during 2019–2020. Water samples were collected in one-litre acid-washed, well-rinsed high-density polyethylene (HDPE) bottles and filtered through 0.45 µm Millipore membrane filter paper. The samples were transported

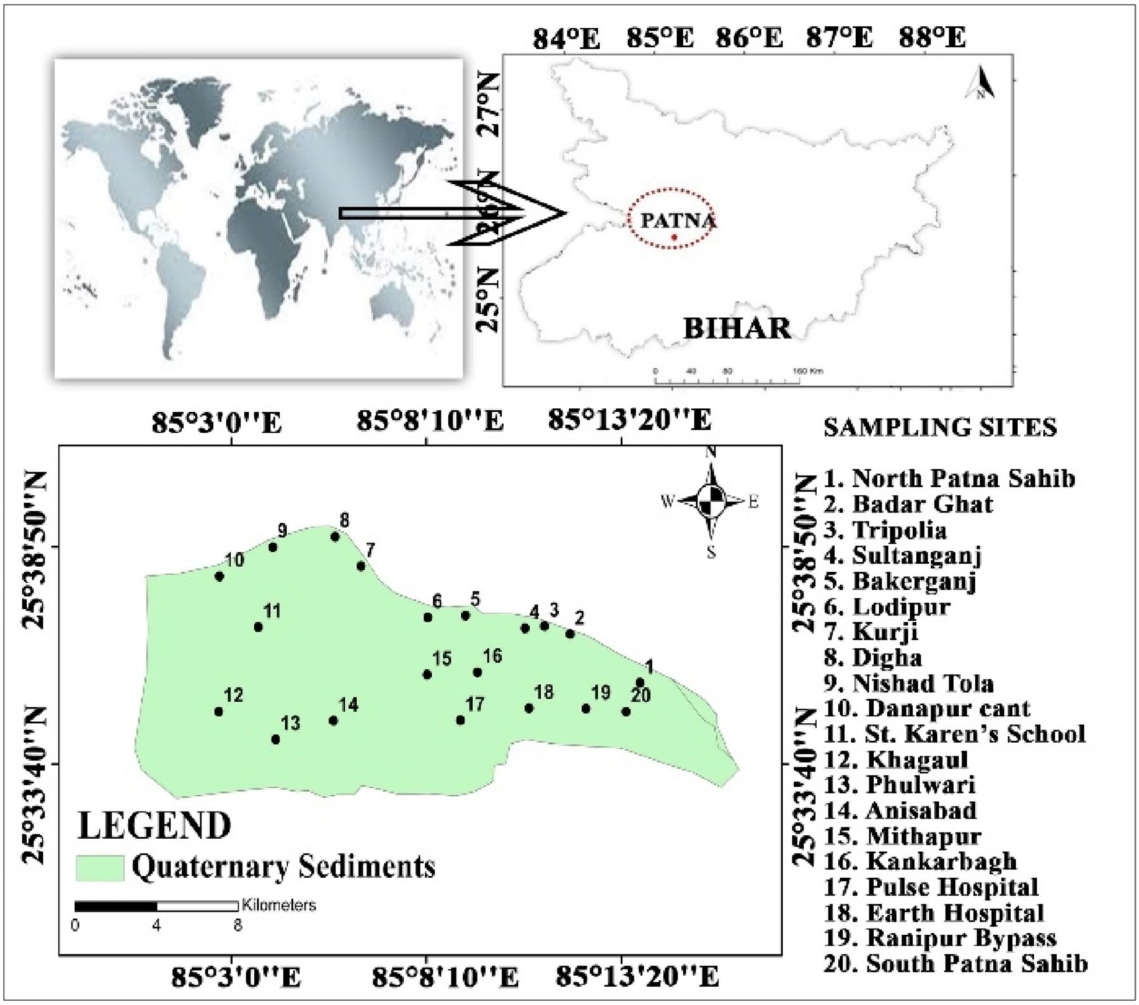

Fig. 1 Geological map of study area showing sampling sites at Patna

to the laboratory in an ice box. The methods given by APHA (2012) were employed in the chemical analysis of samples, and the result obtained was compared with water quality standards prescribed by BIS and WHO. A Portable field kit was used to measure pH, Electrical conductivity (EC) and Total alkalinity (TA) at the sampling sites. The EDTA titrimetric method measured Ca^{2+} and Mg^{2+} ions in the groundwater samples, while the Argentometric and Turbidimetric methods measured Cl^{-} and SO_4^{2-} ions concentration. Na^{+} and K^{+} ions were estimated using Flame Photometer. Each parameter has been analyzed in duplicates, with fresh sample blanks and standards prepared during sample analysis as the quality control of analytical data. Interpretation of the geochemical nature of the groundwater has been carried out using the Piper plot (1944), Durov plot (1948), Gibbs diagram (1970) and Scatter plot diagrams. Piper and Durov plots were constructed using Grapher (version 14.0) software, while an ion Scatter plot was prepared using SPSS (version 22.0) software. Further, the analytical data has been subjected to descriptive statistical analysis, including correlation matrix, principal component analysis, and cluster analysis using XLSTAT (version 14.0) and SPSS (version 22.0).

Result and discussion

Hydro-geochemistry of groundwater

Groundwater samples were analyzed, and the value of physicochemical parameters obtained seasonally, including statistical measures such as minimum, maximum, mean and standard deviation, are presented in Table 1. pH of the groundwater samples varied from 7.1 to 8.1 with an average of 7.3 ± 0.24, indicating a slightly alkaline to alkaline nature of water samples. Electrical conductivity was measured from 300 to 1700 µS/cm, with an average value of 727.5 ± 296.8 µS/cm. The majority of water samples were

Table 1 Summary of physicochemical parameters of groundwater and comparison with BIS Standard

Parameters	PRM			MON			POM			BIS standards (2012)	
	Min	Max	Mean ± SD	Min	Max	Mean ± SD	Min	Max	Mean ± SD	DL	PL
pH	7.3	8.1	7.53 ± 0.24	7.1	7.8	7.27 ± 0.24	7.1	7.7	7.36 ± 0.17	6.5–8.5	6.5–8.5
EC (μS/cm)	300	1300	680 ± 282.10	400	1400	710 ± 290.01	500	1700	790 ± 321.02	750	1500
TH (mg/l)	218	575	303.25 ± 99.22	158	418	240.6 ± 75.23	204	554	318.5 ± 87.54	200	600
Ca^{2+} (mg/l)	61	149	88.95 ± 27.73	17.63	72.48	39.67 ± 13.70	36.07	165.9	71.14 ± 33.17	75	200
Mg^{2+} (mg/l)	3	44	18.45 ± 10.65	14.12	81.81	34.72 ± 17.27	16.07	66.23	34.28 ± 15.55	30	100
HCO^{3-} (mg/l)	260	388	314.65 ± 35.76	250	456	311.8 ± 46.57	228	426	295 ± 54.07	200	600
TDS (mg/l)	236	995	442.15 ± 208.11	262	1188	480.4 ± 258.24	279	1195	465.85 ± 236.74	500	2000
Na^{+} (mg/l)	43	125	83.45 ± 19.30	43.1	102.4	58.24 ± 16.62	43.3	236	67.78 ± 42.70	200	–
K^{+} (mg/l)	3	10.4	5.11 ± 1.83	4.6	14.6	8.24 ± 2.77	5.8	126	14.92 ± 26.27	12	–
Cl^{-} (mg/l)	8	167	49.4 ± 45.84	7	161	47.95 ± 46.50	11	169	54.25 ± 44.91	250	1000
SO_4^{2-} (mg/l)	3	69	27.3 ± 22.68	1	92.2	34.89 ± 32.01	12	113.8	43.52 ± 36.31	200	400

EC electrical conductivity, *TH* total hardness, *PRM* pre-monsoon, *POM* post-monsoon, *MON* monsoon

found to be more than the BIS (2012) prescribed desirable limit (750 μS/cm) for drinking water's electrical conductivity (Table 1).

The higher value of EC in the groundwater might be due to the increased dissolved solids and ions in water (Al Dahaan et al. 2016; Gebresilasie et al. 2021; Zafar et al. 2022). The concentration of TDS ranged from 236 to 1195 mg/l, with an average value of 462.7 ± 231.8 mg/l, indicating the presence of a higher concentration of dissolved salt (Gulgundi and Shetty 2018), and this is also in agreement with higher value of EC. A slight increase in the value of EC and TDS was observed during the end of monsoon and post-monsoon, indicating the dissolution of salts with rainwater infiltrations with local anthropogenic influence (Vidana et al. 2012; Kupwade and Langade 2013; Wagh et al. 2019). The total hardness of groundwater varied from hard to very hard, indicating a high concentration of calcium and magnesium salts (Kumar et al. 2015). The abundance of cations Ca^{2+}, Na^{+}, Mg^{2+} and K^{+} was found in decreasing order (Fig. 2), and mean concentration ranged from 39.67 to 88.95 mg/l, 58.24–83.45 mg/l, 18.45–34.72 mg/l and 5.11–14.92 mg/l for Ca^{2+}, Na^{+}, Mg^{2+} and K^{+} respectively.

The results suggest that $Ca^{2+} + Mg^{2+}$ contributes 63.56% of the total cationic budget, followed by Na^{+} and K^{+} with 33.76% and 2.67%, respectively. Ca^{2+} was dominant among cations because of the dominance of calcium-rich minerals in the earth's crust and its higher solubility (Ali and Ali 2018). An unusual increase in the concentration of Na^{+} and K^{+} was observed during the post-monsoon season at site S20 (Fig. 2) that even exceeded the maximum permissible limit set by BIS (2012), which might be due to the seepage of sewage and domestic wastes into the groundwater. The concentration of anions HCO_3^{-}, Cl^{-} and SO_4^{2-} ranged between 228 and 456 mg/l, 7–169 mg/l and 1–113.8 mg/l respectively. In addition, HCO_3^{-} contributes 71.16% of the total anionic budget, followed by Cl^{-} and SO_4^{2-} with 20.17% and 8.65%, respectively. The concentration of Cl^{-} ion in all water samples of the study area was within the desirable limits prescribed by BIS (2012). However, three samples (S3, S4 and S20) showed relatively higher values throughout the year, possibly due to the seepage of domestic and municipal effluents in the groundwater (Srinivasamoorthy et al. 2014; Kumar et al. 2022a–c). The SO_4^{2-} ion was within their desirable limit (200 mg/l) for drinking water set by BIS (2012).

Hydro-geochemical process

The hydrogeochemical processes that influence groundwater's physicochemical characteristics depend on different relationships between the dissolved ions and processes of weathering of rock present in the earth's crust (Wang and Shao 2013). $Ca^{2+} + Mg^{2+}$ was plotted against $HCO_3^{-} + SO_4^{2-}$ to identify the parental rock responsible for the ion exchange process in the groundwater (Maurya et al. 2019; Kumar et al. 2022a–c). Figure 3a shows that the majority of water, mainly in PRM and MON, was close to the equiline, depicting silicate and carbonate weathering as a significant geochemical process in groundwater (Kumar et al. 2006; Tiwari and Singh 2014; Su et al. 2021) except for those samples, that were well below the equiline, and are indicative of silicate weathering (Bouderbala 2017; Kaur et al. 2019). Apart from that, a significant portion of water during POM falls above the equiline, suggesting reverse ion exchange involvement in contributing Ca^{2+} and Mg^{2+} to the cationic budget (Okiongbo and Douglas 2015; Rao et al. 2015; Subba Rao et al. 2019). $Na^{+} + K^{+}$ ions plotted against $Cl^{-} + SO_4^{2-}$ (Fig. 3b) have revealed that a significant portion of the groundwater of all seasons

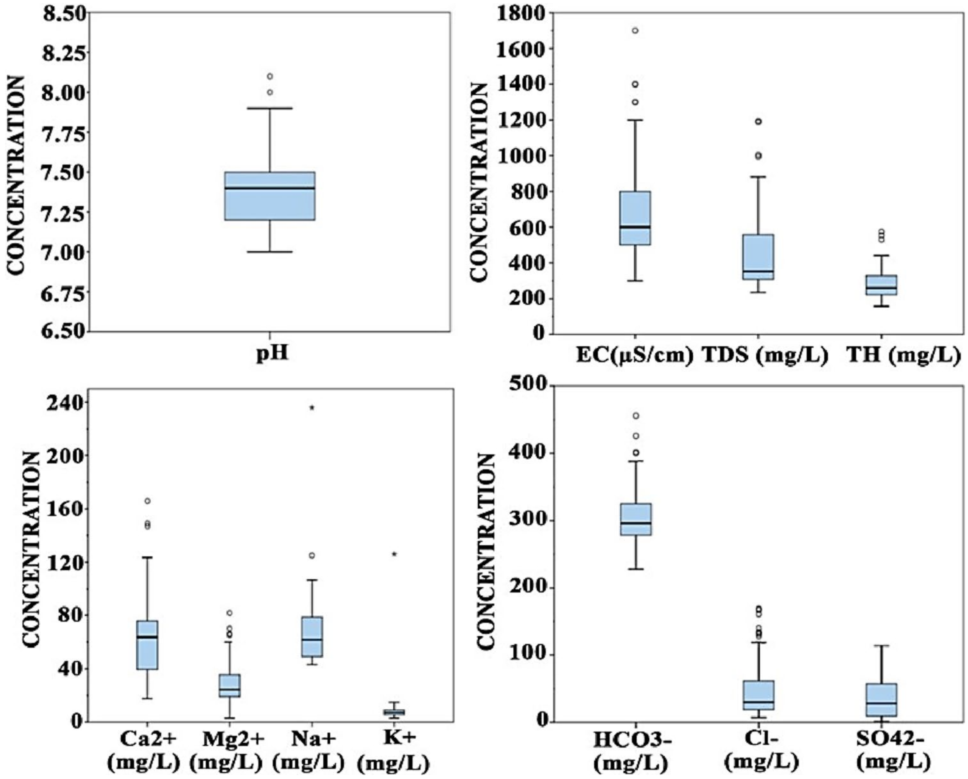

Fig. 2 Box and whisker plot showing the annual variation of physicochemical parameters during the study period (2019–2020)

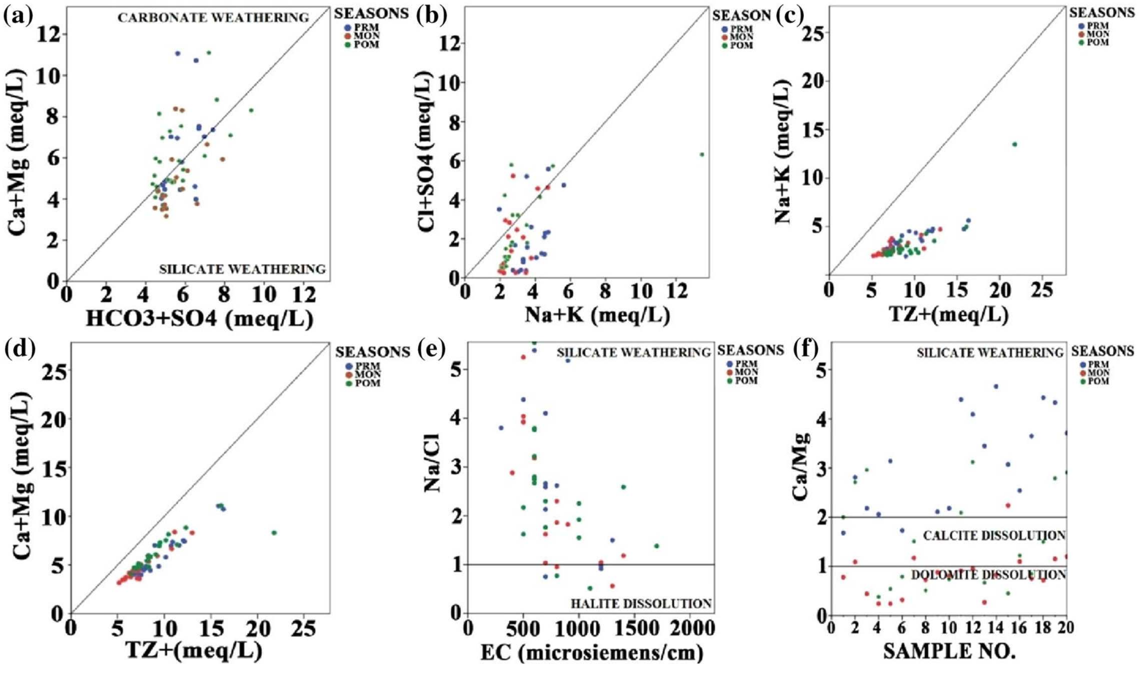

Fig. 3 Scatter plot showing inter ionic relationship between **a** $Ca^{2+} + Mg^{2+}$ verses $HCO_3^{-} + SO_4^{2-}$, **b** $Cl^{-} + SO_4^{2-}$ verses $Na^{+} + K^{+}$, **c** $Na^{+} + K^{+}$ verses TZ, **d** $Ca^{2+} + Mg^{2+}$ verses TZ, **e** Na^{+}/Cl^{-} verses EC, **f** Ca^{2+}/Mg^{2+} verses SAMPLE No

(~79%) plots near and below 1:1 line suggesting mineral dissolution as the process that dominates major-ion chemistry (Zakaria et al. 2021). Few groundwater samples that found their place near or above the 1:1 indicates the dominance of Cl^{-} and SO_4^{2-} and this might be due to the use of fertilizers in agricultural activities (Rajmohan and Elango

2006), use of road salt and from livestock wastes (Kelly et al. 2012). The plot of $Na^+ + K^+$ versus total cations (TZ^+) (Fig. 3c) in all seasons fall below the 1:1 equiline, with an average value ranging from 0.33 ± 0.08 to 0.40 ± 0.007 in different seasons (Table 2), suggests silicate weathering has a significant role that contributes Na^+ and K^+ ions to the water system along with anthropogenic inputs in soil (Stallard and Edmond 1983; Kanagaraj and Elango 2019; Ansari and Umar 2019). Similarly, the ion Scatter plots of $Ca^{2+} + Mg^{2+}$ against TZ^+ (Fig. 3d) revealed the distribution of samples below but close to the theoretical line (1:1). The average value ranged from 0.60 ± 0.07 to 0.67 ± 0.08 in different seasons (Table 2), suggests weathering of silicate and calc–silicate minerals, and reverse ion exchange processes are responsible for ionic characteristics of the groundwater in study area contributing Ca^{2+} and Mg^{2+} ions to the groundwater (Brindha et al. 2020; Pradhan et al. 2022).

An Ion Scatter plot for Na^+/Cl^- against EC was used to examine the influence of evaporation on the groundwater quality. It identifies the source of salinity in the groundwater. A value of Na^+/Cl^- molar ratio equal to 1 suggests halite dissolution is responsible for the release of Na^+ ion to the groundwater, whereas a ratio > 1 indicates Na^+ ion is added to the groundwater from the silicate weathering process (Meyback 1987). The ratio of Na^+/Cl^- in the groundwater of the study area varied from 0.51 to 16.95, with a significant portion of groundwater samples, irrespective of seasons, having a Na^+/Cl^- ratio above 1 (89%), which revealed an excess of Na^+ is introduced to the groundwater system either from silicate weathering or by anthropogenic influences (Li et al. 2018). However, 11% of groundwater samples have a Na^+/Cl^- molar ratio value < 1, indicative of halite dissolution (Fig. 3e). The source of Ca^{2+} and Mg^{2+} in the groundwater environment was determined using an ion Scatter plot of the Ca^{2+}/Mg^{2+} ratio (Mayo and Loucks 1995). A value of $Ca^{2+}/Mg^{2+} = 1$ is indicative of the dissolution of dolomite, whereas a ratio > 1 indicates the dissolution of calcite rock (Mayo and Loucks 1995), and a ratio > 2 signifies silicate mineral dissolution in groundwater (Katz et al. 1997). Figure 3f showed that Ca^{2+} and Mg^{2+} in the groundwater of the study area largely contributed due to dolomite dissolution. A more significant proportion of MON's sample (~ 70%) lies close to the one ratio line, suggesting reverse ion exchange with Na^+ increased Mg^{2+} ions. A similar finding was also observed by (Srinivasamoorthy et al. 2014). Samples that lay well below the 1 ratio line revealed that Ca^{2+} has precipitated as $CaCO_3$, resulting in a decline in Ca^{2+} value during MON and few samples of POM compared to PRM. While most of the water in the PRM season (~ 90%) shows a Ca^{2+}/Mg^{2+} ratio > 2, indicating that silicate dissolution contributes to the Ca^{2+} and Mg^{2+} in the groundwater (Katz et al. 1998). However, few water samples in all three seasons showed a ratio between 1 and 2, indicating the source of ions is from the dissolution of calcite rock. The C-ratio value around 0.50 marks the presence of carbonate termination reaction along with sulfide corrosion, and a value closer to 1, indicates carbonation reactions and atmospheric input of CO_2-deriving protons. The C-ratio (HCO_3–/$HCO_3^- + SO_4^{2+}$) observed during the study period was 0.90 ± 0.07 to 0.94 ± 0.06, showing carbonation reactions along with the atmospheric inputs.

Hydro-geochemical facies

Hydrochemical facies depend on solution kinetics, rock–water interactions, the geology of that area, sources of contamination and flow pattern of the aquifers (Kumar et al. 2023; Zaidi et al. 2019; Liu et al. 2020). It enables us

Table 2 Concentration and ratio of the concentration of different ionic species in the groundwater in Patna during the study period

Parameters	PRM				MON				POM			
	Min	Max	Avg	Std	Min	Max	Avg	Std	Min	Max	Avg	Std
$Ca^{2+} + Mg^{2+}$	3.7	11.07	5.97	2.14	3.17	8.38	4.84	1.52	4.09	11.1	6.38	1.77
$Na^+ + K^+$	1.96	5.62	3.76	0.87	2	4.71	2.76	0.76	2.05	5	3.33	2.51
$HCO_3^- + SO_4^{2-}$	4.58	7.4	5.73	0.86	4.47	7.89	5.47	0.89	4.34	9.34	5.74	1.43
$Ca^{2+} + Mg^{2+}/TZ^+$	0.52	0.78	0.6	0.07	0.49	0.72	0.63	0.06	0.38	0.76	0.67	0.08
$Na^+ + K^+/TZ^+$	0.22	0.48	0.4	0.07	0.25	0.51	0.37	0.06	0.22	0.62	0.33	0.08
Ca^{2+}/Na^+	0.72	3.05	1.27	0.49	0.39	1.55	0.81	0.28	0.6	2.56	1.3	0.46
Mg^{2+}/Na^+	0.07	0.79	0.41	0.18	0.59	2.64	1.13	0.49	0.5	2.53	1.12	0.6
Na^+/Cl^-	0.75	14.81	5.26	4.29	0.56	16.65	4.32	4.3	0.51	6.24	2.79	1.63
$HCO_3^- + SO_4^{2-}/TA^-$	0.54	0.96	0.83	0.12	0.55	0.96	0.83	0.12	0.55	0.93	0.81	0.1
Cl^-/TA^-	0.04	0.46	0.17	0.12	0.04	0.45	0.17	0.12	0.07	0.45	0.19	0.1
$Cl^- + SO_4^{2-}$	0.31	5.57	1.96	1.62	0.26	5.21	1.72	1.59	0.55	6.31	2.44	1.89
C-ratio	0.8	0.99	0.91	0.07	0.84	1	0.94	0.06	0.72	0.95	0.86	0.1

PRM pre-monsoon, *POM* post-monsoon, *MON* monsoon to describe the water quality that differs in chemical composition (Srinivasamoorthy et al. 2014). The concentrations of major ionic species of groundwater for the three seasons were plotted in the Piper diagram in order to identify, classify and compare the water type of the study area (Fig. 4). The diamond-shaped graph in the Piper plot is divided into four different fields based on of hydrochemical facies and nine subfields that identify the combination of distinct cation and anions. The plot revealed that Ca^{2+}–Mg^{2+}–HCO_3^- type water had dominated the study area's groundwater samples, indicating temporary hardness contributed due to sufficient freshwater recharge (Handa 1979; Herojeet et al. 2016). Cationic triangular fields suggest that most groundwater is observed as no dominant cation type in all seasons, with 17% in PRM and 9% in POM, as Ca^{2+} types. Also, 15% of monsoon and 10% of post-monsoon water was Mg^{2+} type, and about 5% of monsoon and post-monsoon groundwater was Na^+–K^+ type. The triangular plot for anions has revealed bicarbonate-type water, suggesting silicate weathering dominance in the study area. Hence, two different types of main hydrochemical facies were observed for groundwater samples, such as Ca–HCO_3 and Mg–HCO_3 dominant in pre-monsoon and post-monsoon and Mg–HCO_3 was observed to be dominant during monsoon season in the study area.

In addition, the Durov diagram was used to extract more information on the hydro-geochemical processes (mixing, ion exchange, reverse ion exchange dissolution) that influence groundwater quality (Aly et al. 2015; Singh et al. 2020). In a Durov diagram, the cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) and anions (Cl^-, HCO_3^-, SO_4^{2-}) values are plotted on two separate ternary diagrams, projected onto a square grid placed at the base of each triangle. The cation triangle suggests that most groundwater is not the dominant cation-type water in all seasons. Based on the classification of Lloyd and Heathcote (1985), 80% (PRM), 76%(MON) and 74% (POM) of the groundwater samples were found in the field 6 indicating the reverse ion exchange process dominated by HCO_3^- and Mg^{2+}. The Remaining water, about 20% in PRM, 24% in MON and 26% in POM, was observed in field 5, indicating that the groundwater exhibits simple dissolution or mixing type with no dominant anion or cation (Fig. 5). This indicates simple dissolution or mixing influence, suggesting recent freshwater recharge that has controlled the geochemical processes in groundwater (Thakur et al. 2018). The HCO_3^- ion surplus in the study area may be due to silicate weathering by carbonic acid in the groundwater (Kumar et al. 2006; Singh et al. 2020). Thus, the Durov diagram revealed weathering of rocks and reverse-ion exchange as two dominant hydrogeochemical processes involved in controlling the groundwater chemistry in the study area.

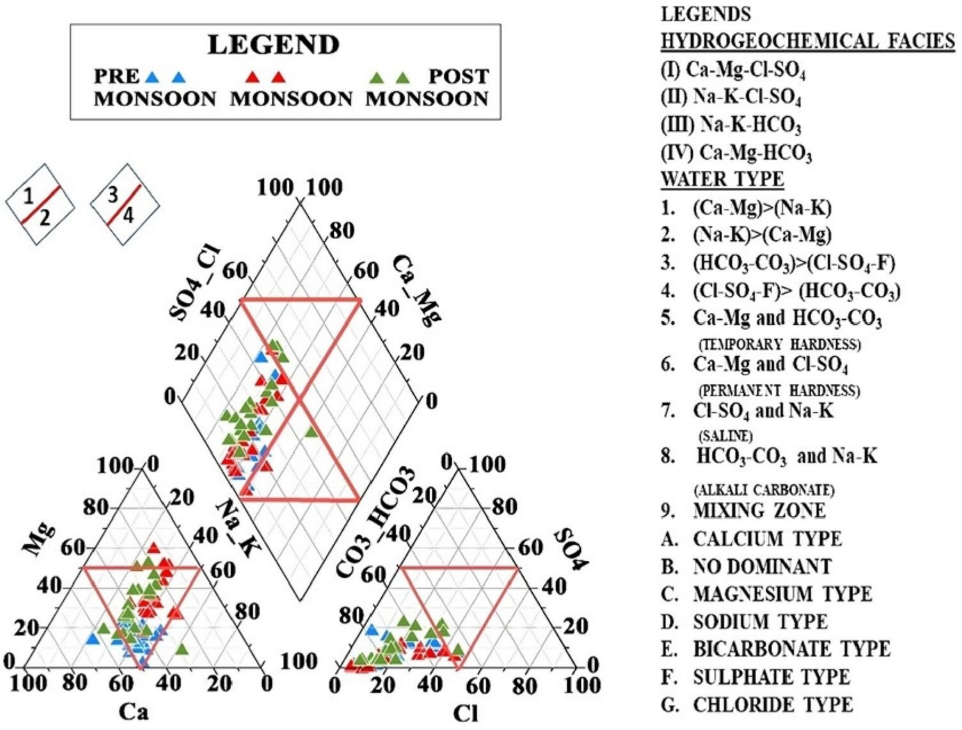

Fig. 4 Piper diagram showing hydro-geochemical facies of groundwater of the study area (2019–2020)

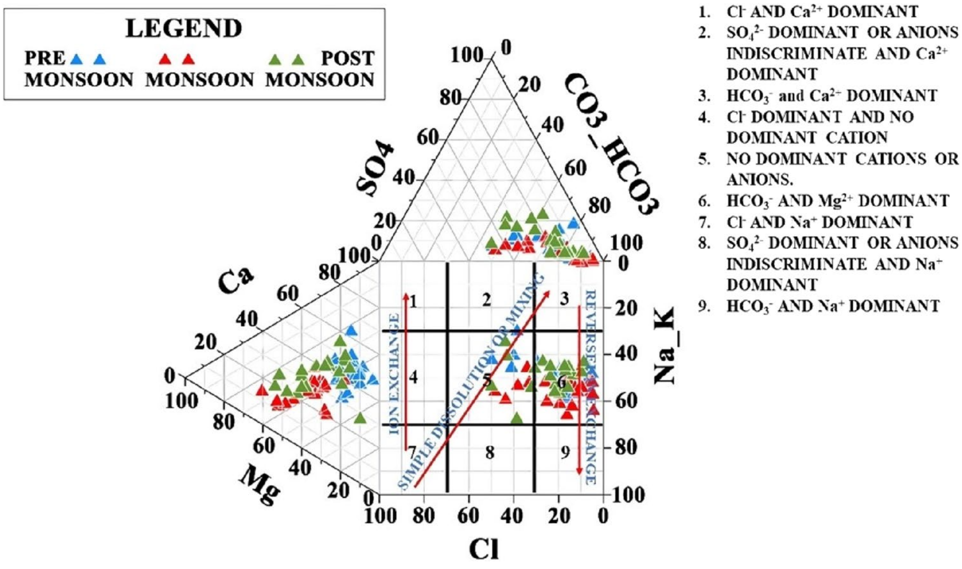

Fig. 5 Durov diagram showing the hydrogeochemical facies involved in the study area

Gibb's diagram was employed to identify hydrogeochemical processes in determining water quality based on the value of TDS and cation/anion ratio to predict the dominant hydrogeochemical factor responsible for groundwater quality. Gibbs ratio was calculated using an equation developed by Gibbs (1970):

$$\text{Gibbs ratio I (for anion)} = \text{Cl}^-/\left(\text{Cl}^- + \text{HCO}_3^-\right)$$

$$\text{Gibbs ratio I (for cation)} = \text{Na}^+ + \text{K}^+/\left(\text{Na}^+ + \text{K}^+ + \text{Ca}^{2+}\right).$$

In this study, the diagram revealed that rock–water interaction involving rock-weathering, dissolution–precipitation and ion-exchange process is the primary source of dissolved ions during all seasons. Furthermore, Gibb's ratio significantly determines water quality (Fig. 6). Very few samples fall in an evaporation–crystallization zone, possibly due to higher TDS resulting from increased chemical weathering and anthropogenic activities (Subba Rao et al. 2019).

Statistical analysis

Correlation matrix

In this study, Pearson's correlation coefficient (r) was employed to identify the relationship between various physicochemical parameters of groundwater, with values ranging between −1 and +1. Correlation coefficient $(r) > 0.7$ suggest a strong correlation, moderate correlation $(0.5 < r < 0.7)$, weak correlation $(0.0 < r < 0.5)$, and no correlation found when $r \sim 0$ (Mudgal et al. 2009) (Table 3).

In our study, TH was strongly correlated with Mg^{2+} (0.830) and Ca^{2+} (0.792) cations, as well as the anions Cl^- (0.903) and SO_4^{2-} (0.717) and suggests the dominant factor responsible for TH are Mg^{2+} and Cl^-. A high positive correlation of TH with Cl^- $(r = 0.903)$ suggests the significant contribution of chloride to non-carbonate or permanent hardness (Chemistry for environmental engineering 1994). TDS was strongly correlated with

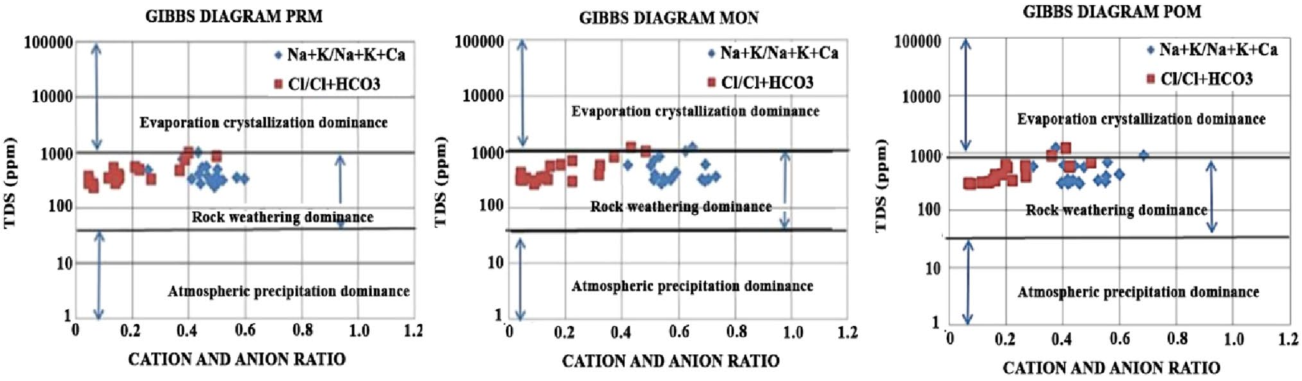

Fig. 6 Gibbs diagram showing controlling factors of groundwater quality

Table 3 Pearson's correlation matrix showing the relation among various physicochemical parameters

Parameters	Ph	EC	TH	Ca^{2+}	Mg^{2+}	TA	TDS	Na^+	K^+	Cl^-	SO_4^{2-}
pH	1										
EC	−0.588	1									
TH	−0.487	0.914	1.000								
Ca^{2+}	−0.477	0.848	0.792	1.000							
Mg^{2+}	−0.411	0.681	0.830	0.346	1.000						
TA	−0.390	0.388	0.360	0.288	0.281	1.000					
TDS	−0.530	0.965	0.924	0.889	0.649	0.376	1.000				
Na^+	−0.353	0.776	0.601	0.636	0.365	0.621	0.732	1.000			
K^+	−0.273	0.511	0.277	0.489	0.014	0.478	0.430	0.789	1.000		
Cl^-	−0.455	0.898	0.903	0.775	0.705	0.328	0.888	0.630	0.488	1.000	
SO_4^{2-}	−0.414	0.824	0.717	0.845	0.363	0.352	0.770	0.663	0.510	0.749	1.000

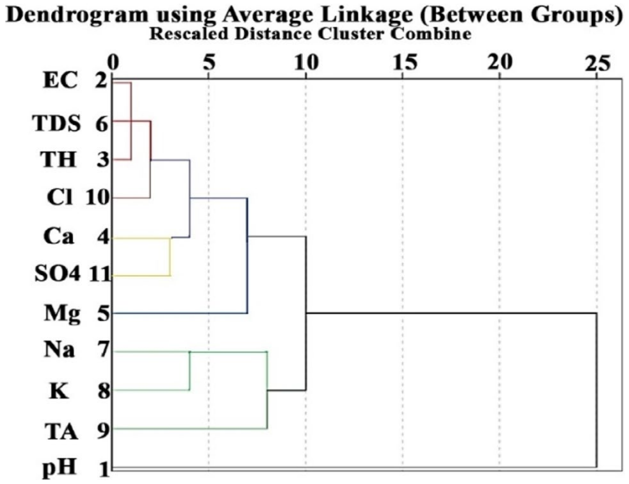

Fig. 7 Dendrogram with clustering results for the physicochemical parameters of the study area during 2019–2020

Ca^{2+} (0.889) and Na^+ (0.732) cations, as well as anions Cl^- (0.888) and SO_4^{2-} (0.770), and it appears that Ca^{2+} and Cl^- are important ions for predicting TDS. Sojobi (2016) and Viswanath et al. (2015) have reported similar results in their study. EC is strongly correlated to TDS (0.965), TH (0.914), Ca^{2+} (0.848), Na^+ (0.776), Cl^- (0.898) and SO_4^{2-} (0.824), and Ca^{2+}, Cl^- and SO_4^{2-} has a significant contribution in EC. The major anion strongly associated with Ca^{2+} is Cl^- ($r = 0.775$) and SO_4^{2-} (0.848), whereas Mg^{2+} are moderately associated with Cl^- ($r = 0.705$), which suggests a similar source origin or geochemical behaviour. A strong correlation between Ca^{2+} and Cl^- ion can be attributed to the dissolution of carbonate rocks and reverse cation exchange of Na^+ ions for Ca^{2+} (Biglari et al. 2016; Mohapatra et al. 2011; Ghodbane et al. 2022). A negative correlation of pH with all parameters explains the minimal contribution of alkaline media in the dissolution process of host rock and soil minerals (Helena et al. 2000). Hierarchical Cluster analysis was further used to analyze the correlation matrix with the help of SPSS software (SPSS version 22.0).

Hierarchical cluster analysis of water parameters exhibited two distinct clusters, as shown in Fig. 7, cluster 1 (C1) comprises two sub-clusters. The First group (Sub-cluster 1) showed a robust correlation between EC, TDS, TH and Cl^- while the second group (Sub-cluster 2) exhibited a close association between SO_4^{2-} and Ca^{2+}, which are ultimately correlated with Mg^{2+}. Sub-cluster I and sub-cluster 2 also showed a strong correlation. Cluster 2 marked a strong correlation between Na^+ and K^+, moderately correlated with TA. The outcomes of HCA confirm the results from the correlation analysis.

Principal component and factor analysis

In the present study, PCA has been carried out on a dataset of groundwater quality parameters using varimax rotation in XLSTAT to understand the problem arising from different measurement scales of the original variable, which is avoided by the diagonalization of the correlation matrix. Results of PCA have been represented in the form of a Scree plot showing principal factors and their eigenvalue together with cumulative variability (Fig. 8a), a score plot showing positive and negative factor loading in groundwater (Fig. 8b) and a loading matrix for different physicochemical parameters for groundwater along with eigenvalue, variability and cumulative percentage summarized in Table 4. PCA results showed that two PCs having eigenvalues > 1 explain 77.44% of the total variance; therefore, these two PCs, namely PC factors1 and PC factors 2 have been taken for consideration (Fig. 8a) since eigenvalues ≥ 1.0, are considered significant (Kim and Mueller 1978). Factor analysis of the study revealed that PC1 describes 63.31% of the total variance and has an eigenvalue of 7.07; therefore, it is considered a primary factor (Table 4). According to Liu et al. (2003), loading signifies "strong" (loading values > 0.75) marked as bold in Table 4, "moderate" (0.5 < loading values < 0.75)

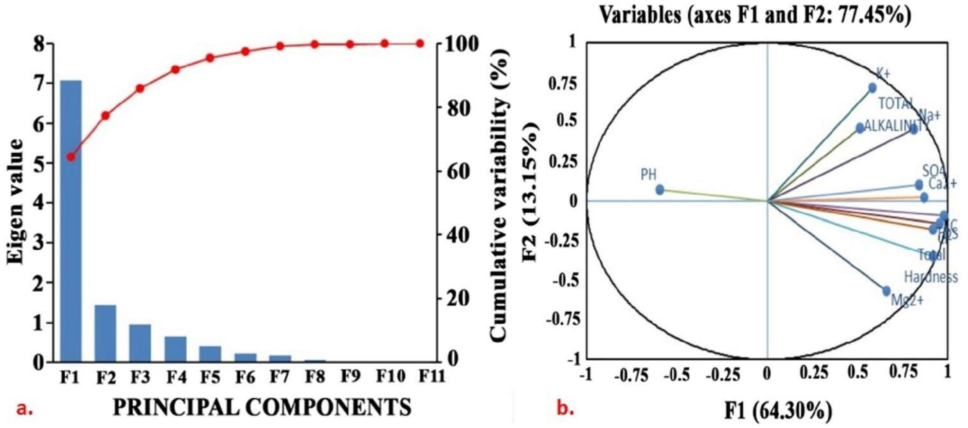

Fig. 8 **a** Scree plot showing principal factors, their eigenvalue, and cumulative variability. **b** Score plot showing positive and negative factor loading in groundwater

and "weak" ($0.3 < \text{loading values} < 0.5$). Therefore, physicochemical parameters having a loading value greater than 0.6 were considered for the interpretation (Singh et al. 2011; Kumar et al. 2022a–c).

PC factor1 showed strong positive loading of EC, TDS, Total Hardness, Ca^{2+}, Na^+, Cl^- and SO_4^{2-}, moderate positive loading of Total Alkalinity and K^+. The value of EC, TDS and TH in the first factor is high, which might be due to the presence of high loading of Ca^{2+} and Na^+ (cations), Cl^- and SO_4^{2-} (anions) in groundwater, which was the dominant factor responsible for EC, TDS and TH. Reghunath et al. (2002) also found that the EC and TDS in the groundwater water of Karnataka were mainly due to Na^+ and Cl^-, though bicarbonate also plays a substantial role in determining EC and TDS. High EC in the water might be due to increased dissolved solids in groundwater (Ahipathi and Puttaiah 2006). PC factor 2, explaining 13.14% of the total variance, has an eigenvalue of 1.44 and shows strong positive loading of K^+, which might be due to the impact of anthropogenic activities from agricultural processes (Kaur et al. 2019) and moderate negative loading of Mg^{2+}. The negative loading of Mg^{2+} and the weak loading of HCO_3^- suggests the removal of magnesium in the form of magnesium bicarbonate precipitate from groundwater. The Bartlett's sphericity test revealed that the observed $\chi^2 = 271.18$ is greater than the critical value $\chi^2 = 73.31$ ('degree of freedom' 55, p values < 0.0001, significance level 0.05) and shows the PCA significantly reduced the dimensionality of the original data (Kumar et al. 2018b, 2019b; Helena et al. 2000).

Table 4 R-mode factor loading matrix for different physicochemical parameters for groundwater along with eigenvalue, variability, and cumulative percentage

Parameters	F1	F2	Initial communality	Final communality
PH	−0.597	0.074	0.684	0.300
EC	**0.978**	−0.094	0.987	0.987
Total hardness	**0.918**	−0.347	0.986	**1.000**
Ca^{2+}	**0.870**	0.021	0.977	0.721
Mg^{2+}	0.660	**−0.564**	0.962	0.624
TDS	**0.956**	−0.142	0.987	0.944
Total alkalinity	0.514	0.460	0.697	0.294
Na^+	**0.812**	0.454	0.940	0.848
K^+	0.582	**0.716**	0.924	0.840
Cl^-	**0.917**	−0.176	0.946	0.854
SO_4	**0.841**	0.101	0.912	0.673
Eigenvalue	7.073	1.446		
Variability (%)	64.300	13.147		
Cumulative (%)	64.300	77.447		

Conclusion

The final section of the study presents preliminary but essential information on the hydrogeochemical characteristics of the groundwater in Patna, which is located in the state of Bihar. The research investigated the regional and temporal differences in the chemical makeup of the groundwater and found that the changing of the seasons had minimal effect on the ionic chemistry of the aquifer. The findings provided substantial evidence that multivariate statistical tools, such as correlation matrices, principal component analyses, and hierarchical cluster analyses, effectively locate the origin of the contamination and forecast geochemical behaviours that are analogous to those found there. Further, it summarizes the principal role of natural and geogenic processes in contributing to the ionic budget of the study area and also identifies deterioration in water quality at some locations as a result of some anthropogenic disturbances. The ionic composition of the groundwater is mainly controlled by the rock weathering process, where mineral dissolution from silicate rocks has dominated the studied region. The result has disclosed the role of cal–silicate and carbonate rock weathering, along with the reverse ion exchange of Ca^{2+} with Na^{+}, to the high concentration of calcium and bicarbonate ions in the groundwater of Patna. It concludes that the Ca–Mg–HCO_3 water type was the dominant hydrogeochemical facies in the groundwater. This study is the most recent and pioneer work in this direction and can be helpful for the authorities concerned to strengthen a sustainable management plan for the study area. However, the study has certain limitations in not estimating the concentration of NO_3^{-}, F^{-} and bacterial load in the groundwater samples. Finally, the study emphasizes regular monitoring of groundwater quality and recommends potential health risk assessment of non-carcinogenic toxicity and trace metal contamination in Patna's groundwater, which can further benefit a comprehensive understanding.

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Authors' contributions MAS, MMZ, RP contributed to Data curation, Formal analysis and investigation, MAS, MMZ contributed to Writing original draft, MAS, MMZ, RK contributed to Software, AK, RKS contributed to Resources, AK, MAS, RK contributed to Writing review and editing, AK, RKS contributed to Editing.

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Data Availability The datasets used or analyzed during the current study are available upon reasonable request from the corresponding author.

Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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