

Groundwater quality and its suitability for drinking and irrigational purpose in Bhojpur district: middle Gangetic plain of Bihar, India

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ABSTRACT

A total of 138, samples have been collected in both pre and post monsoon season to understand the seasonal variability in groundwater quality and its suitability for drinking and domestic water supply. The samples were analysed for physical parameters, major ions along with fluoride and uranium. The results were integrated with GIS to represent both seasonal and spatial variations of groundwater quality parameters, drinking groundwater quality index (DGQI) and irrigation groundwater quality index (IGQI). Results show that groundwater is alkaline in nature and largely controlled by the silicate weathering, ion exchange and reverse ion exchange processes. However high nitrate concentration exceeding the WHO guideline suggests the influence of anthropogenic activities on groundwater quality. The average values of the major ions concentrations was found higher in pre monsoon season due to change in the recharge. The DGQI values of 6 samples in pre monsoon and 2 samples in post monsoon season falls under poor water quality. However, individual irrigation indices along with the combine IGQI indicate groundwater is suitable for irrigation in both the seasons. These results along with the seasonal and spatial variability map may help the decision makers in planning for better domestic and irrigation water supply.

Key words: alluvial floodplain, GIS, groundwater, hydrogeochemistry, water quality indices

HIGHLIGHTS

- Silicate weathering and ion exchange controls ionic species in groundwater.
- High concentration of nitrate in pre-monsoon season suggests influence of anthropogenic activities on groundwater.
- Relatively high ion concentrations are found in pre-monsoon season.
- Groundwater is safe in terms of fluoride and uranium.
- Both DGQI and IGQI suggests that groundwater is safe for drinking and domestic water supply.

1. INTRODUCTION

Groundwater resources play a significant role in economic development and improvement of human health. It is considered as safer in terms of microbial contamination compare to surface water sources but presence of geogenic contaminants has increased the concern over past few decades (Singh *et al.* 2017). The quality of groundwater is often controlled by the regional geology and the aquifer minerals, however, it is vulnerable to the anthropogenic activities. Along with the geogenic contaminants, anthropogenic activities, i.e. rapid urbanisation, unplanned development, improper waste management and other demographic change has also affected groundwater both in terms of its quality and in terms of quantity (Bhatt *et al.* 2021). The quality of groundwater is the most important factor in determining its suitability for drinking, domestic and industrial use. The presence of inorganic contaminants exceeding the World Health Organization (WHO) guidelines has become a major concern for human consumption and other water use (Singh *et al.* 2017; Kumar & Singh 2020). When groundwater moves through its flow path, it interacts with the aquifer minerals through various hydro geochemical processes including weathering, dissolution, precipitation, oxidation-reduction, and ion exchange. These processes majorly determine the ionic

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concentration in groundwater, however, other than these major processes, natural factors such as recharge-discharge zone, residence time, interaction of water with aquifer minerals, surface topography, intermixing of water along with climate plays an important role in determining the ions concentration. Anthropogenic activities, i.e. groundwater exploitation, change in land use/land cover, leaching of fertilizers, agricultural runoff, herbicides, insecticides, pesticides or industrial discharge significantly affects the groundwater quality (Wongsasuluk *et al.* 2014; Badeenezhad *et al.* 2020).

In general, compared to surface water resources, groundwater is not easily contaminated and, at the same time, if contaminated it is difficult to remediate due to inaccessibility and huge volume (Wang *et al.* 2020). As complex hydro-geochemical processes along with the anthropogenic activities may alter the chemical composition of groundwater, it is important to investigate the hydro-geochemical processes and water quality for sustainable economic growth and human health of the region (Kadam *et al.* 2020; Kumar *et al.* 2020; Rao *et al.* 2020).

The quality of groundwater plays a vital role in determining its suitability for human consumption and irrigation water supply. Several methods, i.e. mineral phase equilibrium, stable isotope, chemometric analysis, redox indicator, hydrogeochemical modelling along with conventional graphical methods are extensively used across the globe to understand the groundwater quality and major hydrogeochemical processes responsible for ionic evolution of groundwater (Singh *et al.* 2017; Kumar *et al.* 2020). However, to understand the suitability of groundwater for human and irrigation use national and international guidelines are followed for each of the ions, which may have negative implications on human health or crop productivity. Apart from the individual ions, water quality indices are also used to summarize the overall water quality, which is a numeric integration of large-scale groundwater quality data into a single dimensionless number (Horton 1965). It represents overall water quality at that particular location. Later the indices values are integrated with the GIS to represent the spatial distribution of water quality in the study area. The water quality indices have been compressively used across the globe; however, to make it more inclusive, it has been modified as irrigation water quality index (IWQI), drinking water quality index (DWQI), aquatic life water index (ALWI) and others (Bora & Goswami 2017; Mukate *et al.* 2019; Rao *et al.* 2020). Addition to WQI Kelly ratio (KR), sodium absorption ratio (SAR), sodium percentage (Na%), permeability index (PI), residual sodium bicarbonates (RSB), etc., are also used to determine the suitability of water for irrigation purpose (Abtahi *et al.* 2015; Kumar *et al.* 2020; Bhatt *et al.* 2021).

The study area is the part of the middle Gangetic floodplain under extensive agriculture and the rural population in the study region rely largely on groundwater for their drinking and irrigation use. Quality of shallow groundwater in this region is major concern as arsenic (As) exceeding the WHO guidelines is extensively explored by the several researchers (Acharyya 2005; Donselaar *et al.* 2017; Chakraborti *et al.* 2018; Maity *et al.* 2020; Kumar *et al.* 2021). However, apart from As, very limited studies have been conducted to explore the suitability of groundwater for irrigation and seasonal change in water quality in the study area. With this background, this study is intended to explore the groundwater quality and its suitability for drinking and irrigation purpose. This study excludes As, as a number of studies has been carried out to understand the As geochemistry in the study region. However, this study also explores the baseline uranium and fluoride concentration in the area. Along with the ionic ratio to understand the hydro geochemistry, the indices, i.e. drinking groundwater quality index (DGQI) and irrigation groundwater quality index (IGQI) are used to evaluate the overall water quality. Later, the outcomes are represented with GIS map for better planning and prioritizing efficient management strategies.

2. MATERIAL AND METHODS

2.1. Study area

The study area (Bhojpur district), located in the western part of Bihar state, in the lower middle Gangetic plain of India, dominated by diverse geological formations. The district has Ganga basin in its central parts and it forms the northern boundary of the district. The River Son is flowing at the eastern boundary of the district. It occupies over a total geographical area of 3,395 km²; Figure 1 represents the map of the study area with the corresponding sample locations of two seasons.

The climate of the Bhojpur district is warm and humid. The climate represents a transition between the dry and extreme climates of northern India. In the summer season, the diurnal temperature rises to 44 °C, while in the winter season it drops to as low as 4 °C. The monsoon starts mostly from the middle of June and continues up to the end of September (CGWB 2013).

2.2. Samples collection and field analysis

Grid (6×6 km) sampling method was adopted and a sample from each grid was collected in both pre-monsoon (PRM; March to May 2018) and post-monsoon (POM; October to December 2018) seasons. A total of 138 samples (69 in each season) were

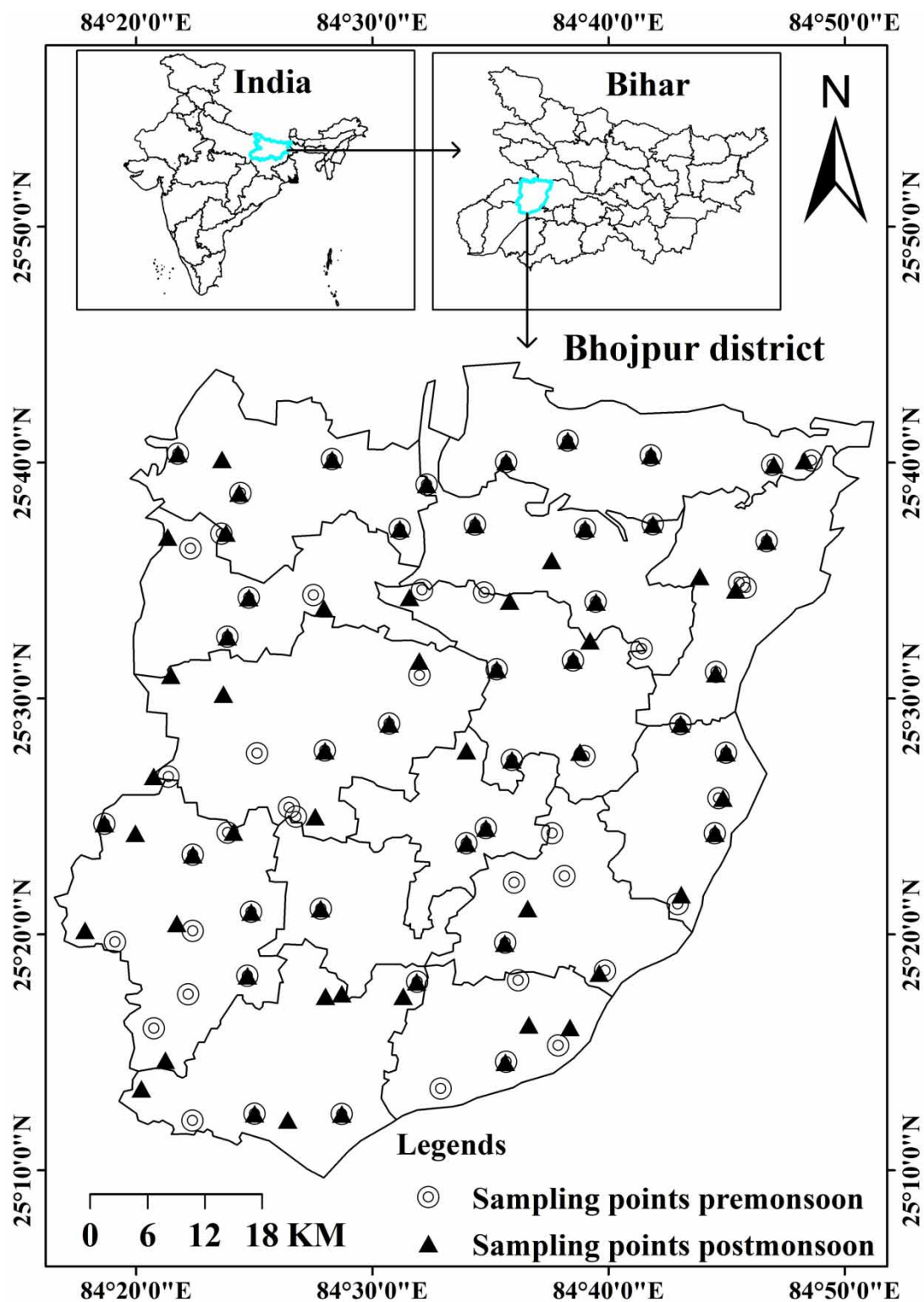


Figure 1 | The map of the study area showing GPS sampling location.

collected and analyzed for major ions including calcium (Ca^{++}), magnesium (Mg^{++}), sodium (Na^{+}), potassium (K^{+}), chloride (Cl^{-}), sulfate (SO_4), nitrate (NO_3), bicarbonate (HCO_3), fluoride (F^{-}) and uranium (U). Before the collection of groundwater samples, hand pumps were purged for 5–6 min to eliminate the influence of iron cast pipe on groundwater quality. The

samples were collected from both private and public wells and the location were recorded using the global positioning system (GPS- Model Garmin Etrex 30x). Field parameters, i.e. pH, total dissolved solids (TDS), electrical conductivity (EC), temperature (T), salinity and oxidation-reduction potential (ORP) were carried out on-site, using a portable digital multi-meter (Thermo Scientific: Orion Star A329). The multi-meter was calibrated for each field parameter using standard calibration solution every day before the use.

Two sets of groundwater samples were collected in prewashed and dried high-density polyethylene (HDPE). Samples for cation analysis was preserved with 6N HNO₃ (Ultrapure Merck), however, the samples collected for anions analysis was kept un-acidified. Both sets of the samples were filled up to the top without any headspace before it was kept in the dry ice packed Styrofoam boxes and transported to a laboratory. In the laboratory, samples were stored at 4 °C and analysed within 10 days of the collection.

2.3. Laboratory analysis

Un-acidified groundwater samples were tested for major anions including F⁻, Cl⁻, NO₃⁻ using ions selective electrodes (ISE; Thermo Scientific: Orion Star A329). However, the concentration of SO₄²⁻ and phosphate (PO₄³⁻) were analysed using UV-VIS Spectrophotometer (Perkin Elmer, λ 25) by turbidity method and stannous chloride method, respectively, using a standard procedure (APHA 2012). Titrimetric method was used for determination of HCO₃⁻ using the measurement of total alkalinity and hardness as per the standard protocol prescribed in APHA (2012).

The major cations such Ca⁺⁺, Mg⁺⁺, Na⁺, K⁺ were determined using titrimetric and flame photometry using a standard procedure (APHA 2012). Replicates for both anion and cations were analysed after every five samples and found within 5%. The total hardness was estimated using the ethylenediaminetetra acetic acid (EDTA) method by titration procedure (APHA 2012). The chemicals, stocks and buffer solutions were analytical grade from Merck India. The progressive standards were made by diluting stock solutions as per the standard protocol (Lachica & Barahona 1993). Additional information such as depth of water, climate and rainfall, soil type and geology were collected from Central Ground Water Board (CGWB) Patna and Indian Meteorology Department (IMD), New Delhi, India.

2.4. Determination of uranium

Uranium concentration was analysed over LED Fluorimeter (LF 2 Quantalase Enterprises Pvt. Ltd, Indore, India), using Fluren buffer solution followed the BRNS standard protocol (Sahoo *et al.* 2010; Ajay *et al.* 2016; Kumar *et al.* 2018; Sahu *et al.* 2020). It is an efficient, precise, and well-established method for detecting uranium levels in aqueous samples, with upper and lower measurement limits of 1,000–0.1 µg/L. The diluted working concentrations were prepared for the regular calibration and testing of the instrument's functioning using a standard stock solution of 100 µg/mL U (Merck India). To minimize matrix distortion as well as other interference by ionic species, water samples were analysed using the standard addition procedure. The double-distilled water was used to prepare the Fluren buffer solution using 5% sodium pyrophosphate reagent and ortho phosphoric acid was used to keep the pH of the buffer solution at 7.0. The prepared reagent solution was then added to the sample water in a 1:10 ratio to transform all of the uranium species together into a single form, resulting in an equal fluorescence yield. The calibration data is provided in the supplementary file.

2.5. Suitability of groundwater for drinking and irrigation use

2.5.1. Drinking water quality index (DWQI)

To assess the suitability of groundwater for drinking purpose, the water quality parameters such as pH, TDS, Ca⁺⁺, Mg⁺⁺, K⁺, Na⁺, SO₄²⁻, Cl⁻, HCO₃⁻, NO₃⁻ and F⁻ were used to calculate drinking groundwater quality index (DGQI). It is an effective indicator of overall water quality and its suitability for drinking water (Rao *et al.* 2020, 2021). DWQI is a numeric method that reduces a large number of water quality parameters in one dimension less value in more scientific and instructive manner to reflect the overall water quality. Calculation of DWQI includes five major steps, (a) assigning unit weightages (in a scale of 1–5) for each parameter based on their significance, (b) calculation of relative weight (*Rw*) using Equation (1), (c) computation of percentage of quality rating (*Qr*) for individual parameters using Equation (2), (d) calculation of

relative rating (R_r) using Equation (3), and (e) aggregation of relative rating for all the parameter.

$$Rw = \frac{Uw}{\sum_{i=1}^n Uw} \quad (1)$$

$$Qr = 100 \times \frac{C}{D} \quad (2)$$

$$Rr = Rw \times Qr \quad (3)$$

$$DGQI = \sum Rr \quad (4)$$

2.5.2. Irrigation water quality index (IWQI)

To assess the suitability of groundwater for irrigation, indicators such as electrical conductivity, sulfate (SO_4^{2-}), and pH were considered. Apart from that, sodium percentage (Na %), sodium absorption ratio (SAR), residual carbonate (RSC), permeability index (PI), magnesium ratio (MR), and Kelly's ratio (KR) are calculated using the formula provided in Table 1. The IWQI was calculated using the similar equation used for DWQI calculation. The values for Uw and Rw were calculated using Equations (1) and (3).

2.6. Spatial distribution and hydro chemical diagram

Spatial distribution (contour) maps were prepared for the spatial association of the chemical properties of data among the sampling locations. These maps were prepared using inverse distance weighted (IDW) raster interpolation and spatial analysis techniques built within ArcGIS 10.1 software. Golden Software Grapher 15 was used to plot Piper trilinear diagram and Chidem (developed by Water Research Centre, Kuwait Institute for Scientific Research) software was used to prepare the Gibbs & USSSL diagram and Doneen's plot.

3. RESULTS AND DISCUSSION

3.1. Ground water chemistry

Based on the pH value, groundwater in the study area is found neutral to alkaline in nature. In PRM season, pH values ranges from 7.1–7.9, however, in POM pH ranges from 6.9–8.8 (Table 2). A slight increase in the maximum pH value is observed during POM that could be imparted due to the high interaction of soil and rainwater (Subramanian & Saxena 1983). Except one sample with pH 8.8, all the groundwater samples in both the seasons are found with the drinking water quality standard, i.e. 6.5–8.5 by WHO. The total dissolved solid (TDS) concentration in groundwater varies from 138–888 mg/L in PRM and 66–912 mg/L in POM with an average of 240 mg/L and 395.8 mg/L, respectively. The variations in TDS concentration in groundwater of the study area suggest multiple hydro-geochemical processes involved in groundwater evolution

Table 1 | Irrigation water quality parameters and formula used for their computation

Parameters	Formula
Sodium adsorption ratio (SAR)	$\frac{Na}{\sqrt{(Ca + Mg)}}$
Residual sodium carbonate index (RSC)	$\frac{(CO_3 + HCO_3) - (Ca + Mg)}{2}$
Permeability index (PI)	$\frac{Na + \sqrt{HCO_3}}{Ca + Mg + Na} \times 100$
Magnesium ratio (MR)	$\frac{Mg \times 100}{Ca + Mg}$
Kelly's ratio	$\frac{Na}{Ca + Mg}$
Sodium %	$\frac{Na + K}{Ca + Mg + Na + K} \times 100$

Table 2 | Descriptive statistics of groundwater in the study area in both seasons (PRM & POM)

Parameters	Mean		Median		Mode		Std. Devi.		Range		N > WHO limit	BIS/WHO limits
	PRM	POM	PRM	POM	PRM	POM	PRM	POM	PRM	POM		
pH	7.47	7.3	7.5	7.3	7.5	7.2	0.18	0.3	7.1–7.9	6.9–8.8	0	6.5–8.5
TDS	240.2	395.8	372	360	378	354	135	144.8	138–888	66–912	0	1,000
EC	670.3	659.7	620	600	630	590	225	241.4	230–1,480	110–1,520	0	1,400
ORP	112.3	165.3	125	210.7	211	–	89.3	97.9	–56.3–256.9	–51.7–291.2	0	–
Salinity	388	324.8	363	297.3	364	–	142	125.9	180.3–786.2	70.3–768.4	0	–
DO	2.71	2.7	2.66	2.3	2.1	1.9	0.7	1.4	1.35–4.77	1.11–10.18	0	–
F [–]	0.46	0.3	0.38	0.3	0.25	0.2	0.2	0.2	0.12–1.15	0.09–1	0	1.5
Cl [–]	18.98	26.2	6.8	8	13.2	10	23	23.9	0.3–104	3.0–100	0	250
NO ₃ [–]	59.22	9.2	59.2	5.2	60.1	2.7	12.4	9	26.7–91.3	0.87–50.7	53	45
SO ₄ ^{2–}	12.91	16.6	5.87	9.08	1.4	3	14.2	17.9	0.42–65.18	1.86–84.26	0	200
PO ₄ ^{3–}	0.3	0.1	0.24	0.08	0.3	0.06	0.1	0.2	0.00–0.68	0.00–1.35	0	–
U [–]	2.44	2.3	2.11	2.1	2.1	0.1	1.4	2	0.09–8.61	0.1–7.49	0	60 (AERB)
TH	289	269	280	252	260	236	77.3	88.7	100–544	144–668	0	200
HCO ₃ [–]	89.17	83	91	80	90	80	19.5	23.5	38–142	40–170	0	300
Ca ⁺⁺	72.1	73.35	67	67.7	58.9	61.8	21.7	23.4	23.5–140.5	41.9–171.5	0	–
Mg ⁺⁺	26.5	20.9	25.7	18.8	17.2	15.1	10.9	10	1.3–56.38	5.6–58.3	0	–
Na ⁺	217.5	272.1	187	239.1	290	–	116	101.8	59.39–582.7	94.5–590.6	32	200
K ⁺	31.2	12.5	19	12	10.4	7.5	27.8	7.5	1.89–131.92	1.04–39.6	32	20

All the values are in mg/L except pH, EC ($\mu\text{S}/\text{cm}$) and U ($\mu\text{g}/\text{L}$).

(Subba Rao *et al.* 2020). Based on the total dissolved solid concentration, all the groundwater samples collected from the study area are found under freshwater category (Subba Rao *et al.* 2017), however, 13 and 15% groundwater samples exceeds the WHO guidelines of 1,000 ppm in PRM and POM seasons, respectively. Electrical conductivity (EC) of the groundwater samples are found within the permissible limit except 1 in POM with EC value 1,520 $\mu\text{S}/\text{cm}$ (Figure 2(a)). A large variation in EC is observed as it ranges from 230 to 1,480 $\mu\text{S}/\text{cm}$ with an average of 670 $\mu\text{S}/\text{cm}$ in PRM, however, in POM it ranges from 110 to 1,520 $\mu\text{S}/\text{cm}$ with an average of 659 $\mu\text{S}/\text{cm}$ (Table 2). The EC values <1,500 $\mu\text{S}/\text{cm}$ suggests dominance of rock water interaction, however, the wide variation demonstrates different geochemical processes responsible for high ionic activities in study area. Wide variation in oxidation-reduction potential (ORP) is observed as it varies from –56.3 mV to 291.2 mV, however, the higher ORP is observed in POM season. However, there is no change in the average DO values as it is found to be 2.7 ppm in both seasons. ORP and DO are commonly used parameters for governing the aeration methods; they also have a significant role in oxidation-reduction processes involved in governing groundwater chemistry (Bjugstad *et al.* 2016). High ORP in POM season might be due to increase in mixing of surface water during the post-monsoon season.

Based on the average concentration, Na⁺ is found as the most dominant cation followed by Ca⁺⁺ > Mg⁺⁺ > K⁺ in both the season. In the groundwater system, cations are mostly contributed due to the interaction between groundwater and aquifer minerals through geochemical process such as weathering, ion exchange, dissolution and precipitation (Singh *et al.* 2017; Bhatt *et al.* 2021). The concentration of Na⁺ varies from 59.39 to 582.7 mg/L with an average of 217.5 mg/L in PRM, however; in POM it is found 94.5–590.6 mg/L with an average of 272.1 mg/L, respectively. A total of 33 samples in PRM has high concentration of Na⁺, exceeding the WHO guidelines, however, 54 samples exceeds the WHO guidelines during POM season. A high concentration of Na⁺ in groundwater exceeding WHO guidelines may cause hypertension in humans (WHO 2011), while if used for irrigation, it may reduce the soil fertility (Bauder *et al.* 2011). Na⁺ is conservative in nature and it binds with the clay minerals owing to ion exchange (Subramanian & Saxena 1983), however, poor drainage condition are also an additional source of Na⁺ ion in groundwater (Subba Rao *et al.* 2017, 2021). Calcium (Ca⁺⁺) in groundwater is contributed through the weathering of calcium bearing minerals such as calcite, fluorite, calcium feldspar, amphibole, apatite, etc. The Ca⁺⁺ concentration in groundwater ranges from 23.5 to 140.5 with an average of 72.1 mg/L

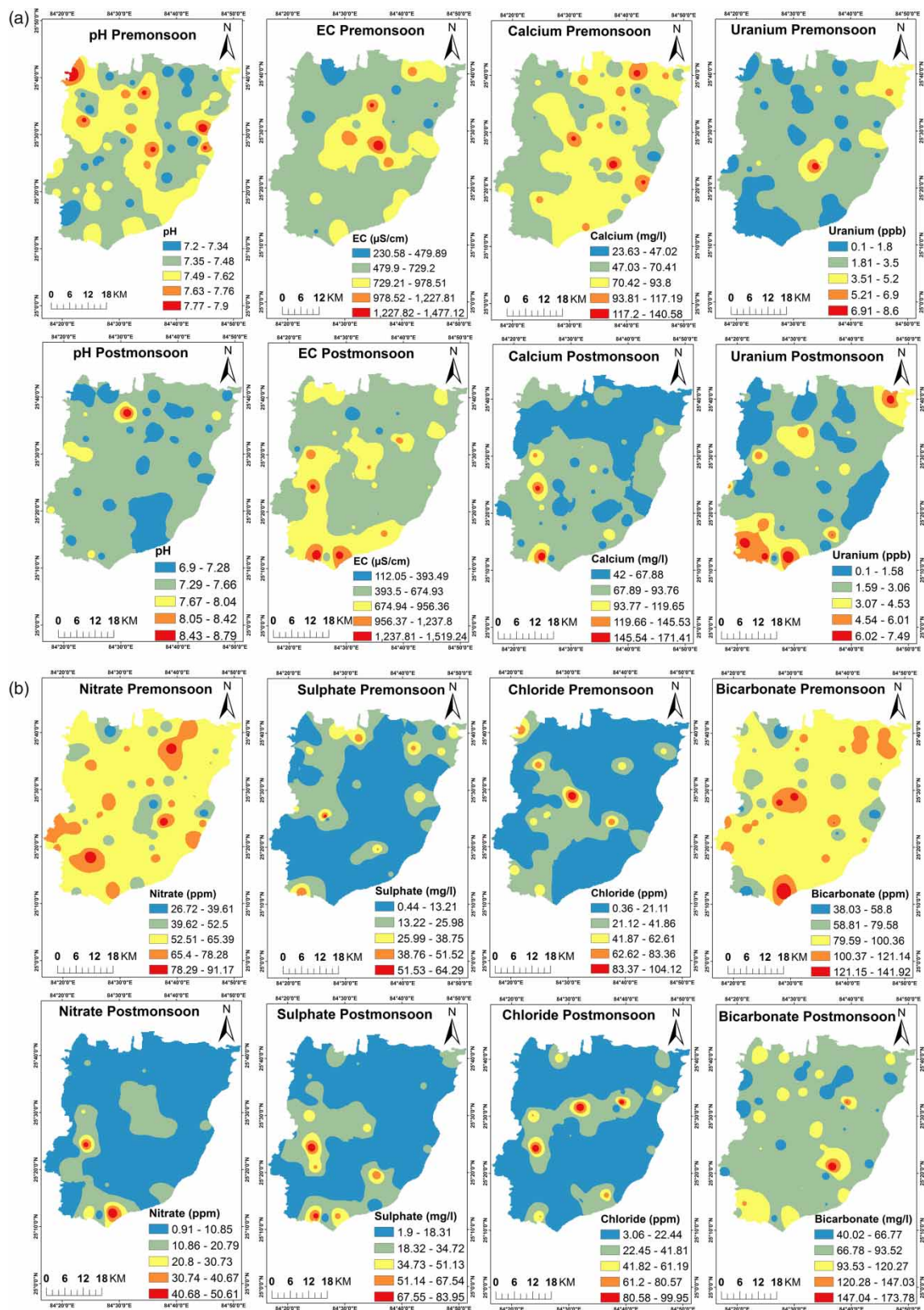


Figure 2 | (a) Spatial and seasonal variation of pH, EC, Ca, U in the study area. (b) Spatial and seasonal distribution of major anions in the study area.

in PRM, however, 41.9–171.5 in POM, respectively (Figure 2(a)). Ca^{++} along with Mg^{++} and HCO_3^- ions determines the hardness of groundwater (Singh *et al.* 2017). Mg^{++} concentration in groundwater varies from 1.3 to 56.38 mg/L and 5.6 to 58.3 mg/L in both PRM and POM, respectively. Ca^{++} and Mg^{++} ions precipitate in the soil zone resulting in temporary hardness in the groundwater. As the deposited salts get washed away from the soil by rainwater which contributes to an increase of these ions in the groundwater during POM season. High concentration of Mg^{++} in irrigation water may reduce the fertility of the crop by reducing the uptake of Ca^{++} and K^+ ions. High concentration of K^+ ion in groundwater is observed during the PRM, as 43.6% of collected groundwater samples have high K^+ exceeding the WHO guideline, however, in POM 17.3% of the samples exceed the WHO guidelines. Orthoclase feldspar are the natural source of K^+ ion in groundwater, however, it is mostly contributed through the agricultural runoff containing the excess of potassium fertilizers used in agriculture.

Among the major anions, Cl^- is found as the most dominant one followed by HCO_3^- , NO_3^- and SO_4^{2-} . Concentration of Cl^- ions ranges from 0.3 to 104 mg/L with an average of 18.98 mg/L in PRM however it varies from 3.0 to 100 mg/L in POM with an average of 26.2 mg/L (Table 2). High concentration of Cl^- in groundwater is mostly attributed due to the climatic factor such as high evaporation; however, additionally domestic wastes, seepage from septic tank, and irrigation return flow might also contribute Cl^- in groundwater (Kumar & Singh 2015). The HCO_3^- in groundwater ranges from 38–142 mg/L with an average of 89.3 mg/L in PRM; however, in POM it ranges from 40–170 mg/L with an average of 83 mg/L (Figure 2(b)). HCO_3^- along with Ca^{++} and Mg^{++} in groundwater determines the hardness of groundwater. The concentration of HCO_3^- in groundwater is mostly attributed due to the soil water interaction during the recharge process; however, other processes such as root respiration along with the degradation of organic matter might also attribute HCO_3^- in groundwater. The study area is a part of organic rich fertile alluvial floodplain with extensive agriculture; the decomposition of organic waste from agriculture might be the major reason for HCO_3^- enrichment (Singh *et al.* 2017; Kumar & Singh 2020).

The concentration of NO_3^- has ranged from 26.7 to 91.3 mg/L with an average of 59.2 mg/L in PRM; however, it varies from 0.87 to 50.7 mg/L with an average of 9.2 mg/L in POM. Anthropogenic activities such as leaching of fertilizers and agricultural runoff along with the leakages from septic tank and municipal waste are considered as the major source for NO_3^- . High concentration of NO_3^- is observed in PRM season, which might be due to the standing crop and fertilizers application during PRM season.

Fluoride (F^-) concentration in groundwater of the study area varies from 0.12 to 1.15 mg/L in PRM with the mean of 0.46 mg/L; however, in the POM it ranges from 0.12 to 1.15 mg/L with an average of 0.3 mg/L. Groundwater in the study area is found safe with respect to the fluoride contamination, but in the majority of the samples F^- is found to be below the recommended limit, which may pose a significant health risk.

3.2. Hydro-geochemical processes

The chemical composition of groundwater largely depends on the interaction of groundwater and the aquifer minerals through various hydrogeochemical processes, i.e. weathering, precipitation, dissolution, evaporation and ion exchange. To understand the dominance of major ions in groundwater, piper diagram is used; it summarizes the geochemical attributes and the hydrogeochemical characteristics of groundwater (Piper 1944). The piper diagram indicates that in both the seasons' groundwater quality is mostly dominated by Mg^{++} followed by Na^+ ions; however, among anions, HCO_3^- ions are dominant in both the seasons (Figure 3).

The dominance of cations, i.e. Mg^{++} and Na^+ , suggests the weathering of aquifer minerals and ion exchange; however, dominance of bicarbonates is due to root respiration and decomposition of high organic matter (Kumar & Singh 2020).

To understand the major hydrogeochemical processes governing the groundwater quality of the study area the ionic species are plotted against the total dissolved solid concentration (Gibbs 1970). The plot indicates that in both PRM and POM seasons, the groundwater quality is highly influenced by the weathering of aquifer minerals, i.e. the rock water interaction (Figure 4).

The scatter plot between HCO_3^-/Na and Ca/Na suggests that the groundwater of the study area is highly influenced by weathering of silicate minerals (Figure 5(a)). In general, the dissolution of dolomite and calcite minerals are responsible for high Ca^{++} and Mg^{++} along with HCO_3^- ions in groundwater. However, as the study area is alluvial floodplain of River Ganga with dominant agriculture, other processes such as root respiration and decomposition of organic matter might also contribute to high HCO_3^- in groundwater (Mukherjee *et al.* 2011; Diwakar *et al.* 2015; Kumar & Singh 2020). Scatter plot between Mg/Na and Ca/Na also suggests silicate weathering as the dominant process and the major contributor of Mg ion in groundwater (Figure 5(b)).

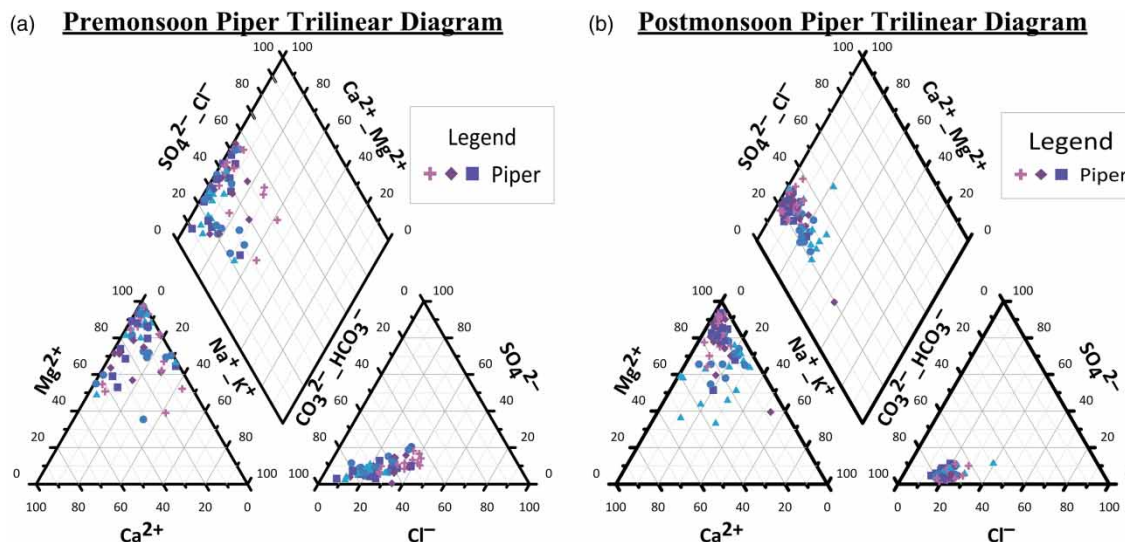


Figure 3 | Piper trilinear diagram (a) PRM and (b) POM.

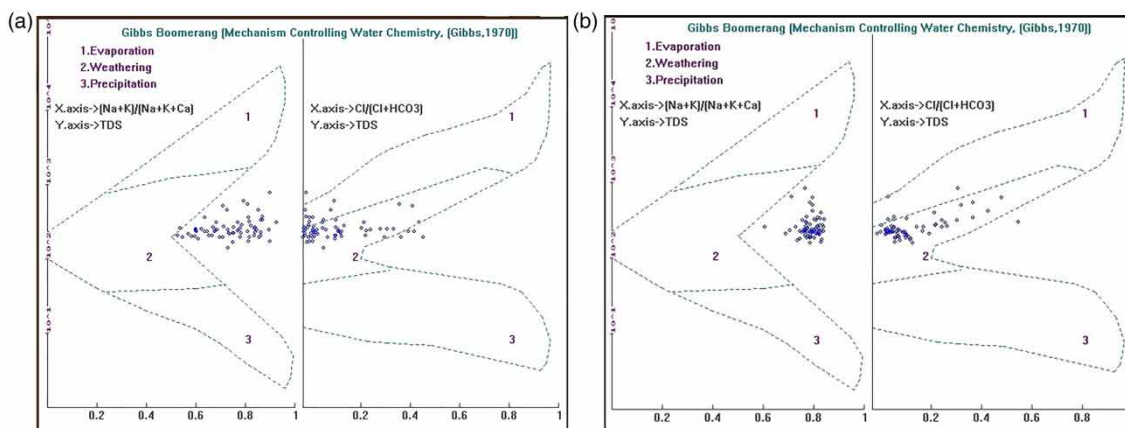


Figure 4 | Gibbs diagram (a) PRM and (b) POM.

Scatter plot between $\text{Ca}+\text{Mg}$ vs. SO_4+HCO_3 is used to infer the ion exchange process. If the samples are close to the equiline, it suggests the dissolution of dolomite, calcite or gypsum. However, in case of reverse ion exchange, the samples will have excess Ca^{++} and Mg^{++} and it will tend to shift the points towards the left. In this study, both ion exchange and reverse ion exchange have significant impact on groundwater quality (Figure 5(c)). The scatter plot between Na^+ and Cl^- is used to understand the ion exchange process. The high values of Na^+ in groundwater of the study area indicate the contribution of Na^+ from other sources apart from the halite dissolution (Figure 5(d)). The chloro-alkalinity indices (CAI) are an indicator of a specific ion exchange process in groundwater. CAI-I and CAI-II are calculated using Equations (5) and (6).

$$\text{CAI I} = \frac{\text{Cl}^- (\text{Na}^+ + \text{K}^+)}{\text{Cl}^-} \quad (5)$$

$$\text{CAI II} = \text{Cl}^- - (\text{Na}^+ + \text{K}^+ + \text{SO}_4^- + \text{HCO}_3^- + \text{CO}_3^- + \text{NO}_3^-) \quad (6)$$

In the case of negative values of CAI I and CAI II, it suggests that the Na ions absorbed on the surface of aquifer minerals will be replaced by Ca^{++} or Mg^{++} ions which will contribute Na^+ in groundwater. However, the positive values of CAI

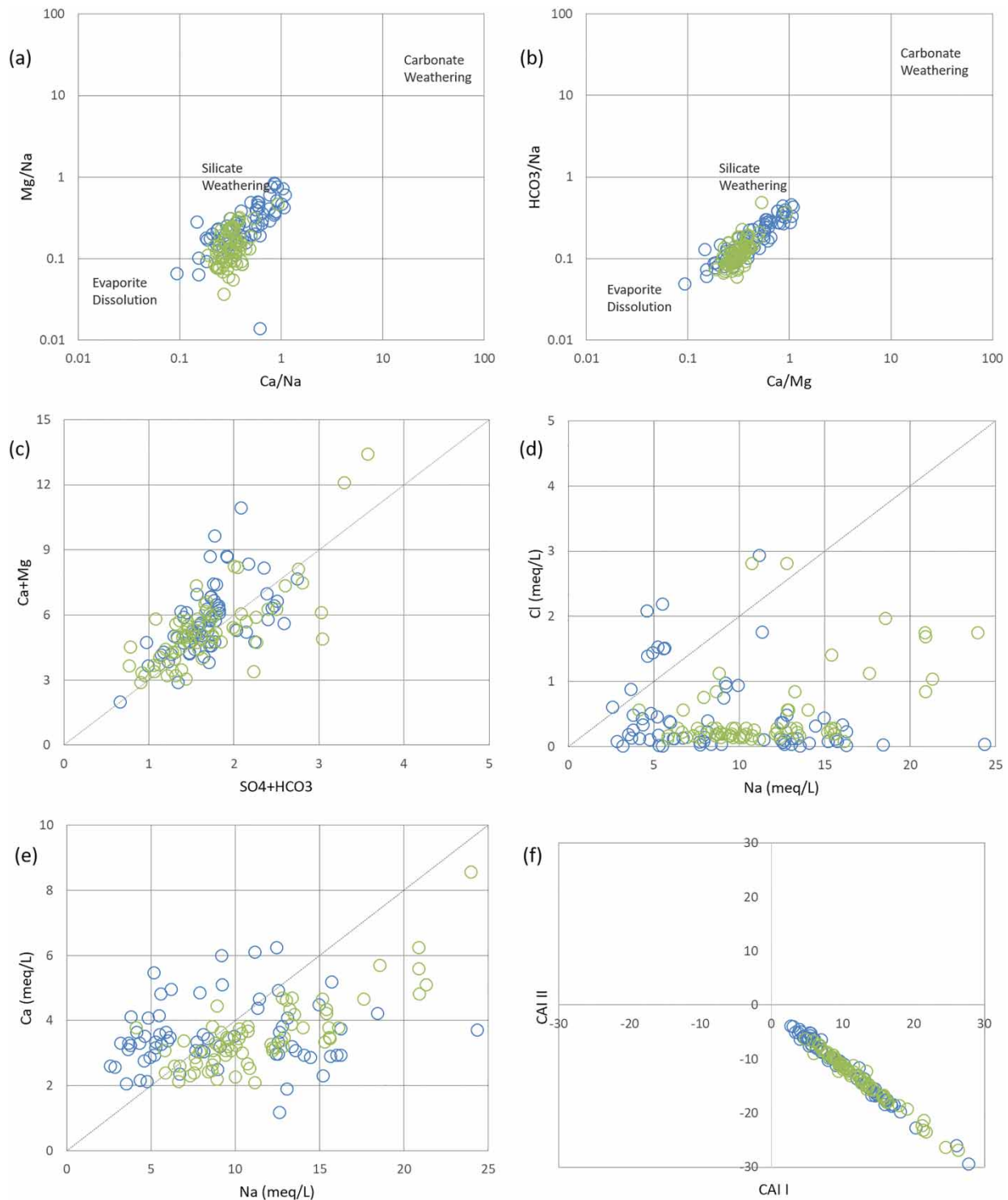


Figure 5 | (a) Scatter plot between HCO_3^-/Na and Ca/Na . (b) Scatter plot between Mg/Na and Ca/Na . (c) Scatter plot between $\text{Ca}+\text{Mg}$ and SO_4+HCO_3 . (d) Scatter plot between Cl and Na ions. (e) Scatter plot between Ca and Na ions. (f) Scatter plot between Chlro Alkalinity indices I and II.

indicate the exchange of Na^+ from groundwater by the Ca^{++} or Mg^{++} ions from the aquifer mineral. As represented in Figure 5(f), all the groundwater samples fall on the lower right panel, indicating influence of both ion exchange and reverse ions exchange in processes in the study area (Figure 5(f)).

3.3. Suitability of water for human use

The suitability of groundwater is assessed using the DWQI, a dimensionless value which classifies groundwater into five major groups: 1) excellent with $DWQI < 50$, 2) good with $DWQI 50-100$, (c) poor with $DWQI$ values $100-200$, (d) very poor with $DWQI 200-300$ and (e) not suitable for human use with $DWQI > 300$. In the current study, the $DWQI$ values vary from 43 to 135 with an average of 73 in PRM season. In total, five out of 69 samples belong to the excellent water quality, 58 out of 69 belong to good water quality, and six out of 69 samples are categorized under poor water quality. However, in POM season, the $DWQI$ value ranges from 30 to 112 with an average of 53. In total, 37 out of 69 samples fall under excellent water quality, 30 out of 69 under good water quality and two samples fall under poor water quality. None of the groundwater samples collected from the study area were very poor or not suitable for human consumption.

As agriculture is the most dominant human activity in the study area, the groundwater quality for irrigation is evaluated using indices such as sodium absorption ratio, residual sodium carbonate, permeability index, magnesium ratio and Kelly index (Table 1). The values of these indices suggest suitable groundwater quality for irrigation. However, these individual indices were used to assess the overall groundwater for irrigation (IWQI) (Subba Rao 2020). The values of IWQI can also be classified into five major classes: (1) IWQI < 50 : excellent; (2) IWQI $50-100$: good; (3) IWQI $100-200$: poor; (4) IWQI $200-300$: very poor and (5) IWQI > 300 : not suitable for irrigation. The groundwater quality in the study area is found suitable for irrigation as all the samples except one in both POM (101) and PRM (110) have IWQI values < 100 .

To obtain a more comprehensive assessment of irrigation waters quality, a USSL classification diagram can be used. Water is classified into 16 classes using the USSL diagram, which shows sodium risks (SAR) on the y-axis vs. salinity hazards (EC) on the x-axis (log scale). While classifying irrigation water, the USSL diagram best explains the combined effect of sodium and salinity hazards. As a result of the combined effect of sodium and salinity hazards, the curves may be interpreted.

The USSL diagram showed that all of the water samples fall into the categories of C2S1 (water with a low salinity may be utilised to irrigate most crops on most soils but there will be a certain amount of leaching required), C2S2 (it is possible to cultivate plants with moderate salt tolerance in most cases without the need of specific techniques to regulate salinity) and C3S1 (plants with intermediate salt tolerance growing in soils with moderate permeability and leaching) and C3S2 (water with a high salinity cannot be utilised on soils with poor drainage) (Figure 6). This implies that the groundwater has a moderate to low sodium danger and a medium salinity.

4. CONCLUSION

The present study investigates the groundwater quality and its suitability in middle Gangetic floodplain. The majority study area is under agriculture and groundwater is extensively used for domestic and irrigation water supply. The results of this study infers that the groundwater quality is controlled by both natural and anthropogenic activities. Hydrogeochemical processes such as silicate weathering along with ion exchange and reverse ion exchange have major control over ionic species in both the seasons, however, anthropogenic activity such as agricultural runoff also influences the groundwater quality especially in post-monsoon season. Na-HCO_3 is found as the dominant water types in both pre- and post-monsoon seasons.

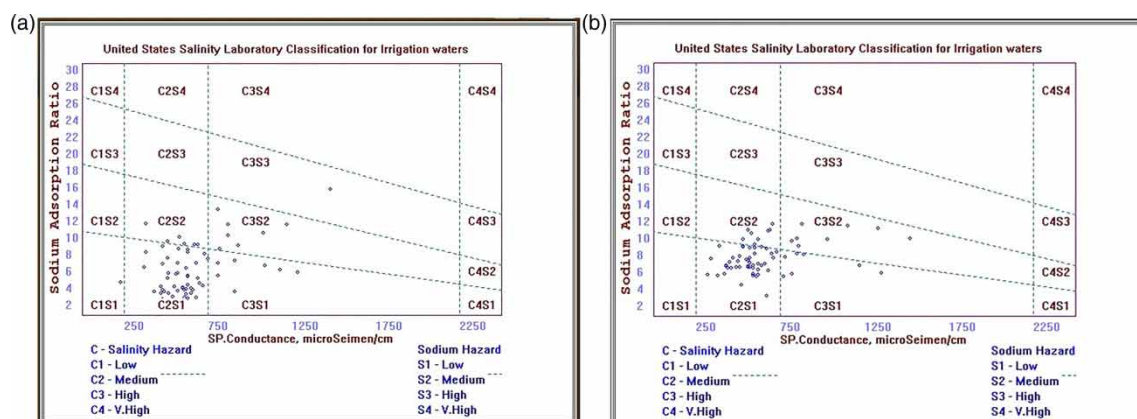


Figure 6 | USSL diagram (a) PRM and (b) POM.

Based on the WHO guidelines, the excess of NO_3^- concentration at 53 sampling location along with K^+ and Na^+ ions exceeding at 35 locations, makes it unfit for drinking. However, groundwater of the study region is found safe in terms of uranium and fluoride ions investigated in this study. Based on both irrigation and drinking water quality indices, groundwater of the study region is found suitable for human consumption and irrigation water supply. The USSL diagram infers most groundwater has low salinity–low sodium danger or medium salinity–low sodium hazard. There is a need of continuous monitoring of wells in this region before use. The findings of this study along with the spatial-temporal map may help in effective management and supply of groundwater for drinking and irrigation purpose.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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