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Isotopic signature in integration with hydrochemistry to infer the groundwater quality in alluvial aquifer, Jhajjar district, Haryana, NCR, India

Rina Kumari (rina.sesd@cug.ac.in)
Central University of Gujarat https://orcid.org/0000-0003-1824-6351
Sudhir Kumar
National Institute of Hydrology
Mavidanam Someshwar Rao
National Institute of Hydrology Central India Hydrology Regional Centre
Saumitra Mukherjee
Jawaharlal Nehru University
Ratan Sen
Jawaharlal Nehru University

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Abstract

In many Asian megacities, millions of human inhabitants are dependent on groundwater for fulfilling daily water demand due to lack of public water supply and infrastructure. Many of these megacities are situated on alluvial plains which are more susceptible to contamination also. The present study has been carried out in Jhajjar District, Haryana, a part of Indo-Gangetic Plain, India.

Indo-Gangetic plain, harbour one of the most productive alluvial aquifer of the world and plays an important role in Indian economy. After green revolution, in a large part of Indo-Gangetic plain groundwater salinization and contamination has been reported. In past few decades, groundwater in Jhajjar district is continuously degraded by fluoride, sulphate, chloride, salinity, etc. problems. So, the present study aims to assess the groundwater quality of the alluvial aquifer of Jhajjar district using integrated approach. Hydrochemistry in integration with stable isotopes ($\delta^{18}O$ and δD), GIS and multivariate statistical analysis has been to decipher the sub-surface geochemical processes taking place. Twenty-one groundwater samples were collected and a total 14 hydro-chemical parameter and water stable isotopes ($\delta^{18}O$ and δD) has been analyzed. Hierarchical clustering of hydro-chemical and isotopic data classified the water in three groups, varying from fresh to brackish/salt waters. Sampling location with higher salinity is showing enriched fluoride signature. Depletion in water level, insufficient flushing with freshwater is affecting fresh-saline water interface which favors the dissolution and mobilization of salts from the unsaturated zone as well as pollution in aquifer. Understanding the recharge processes and the groundwater dynamics is critical to assess the vulnerability and protection of groundwater resources.

1. Introduction

The increasing imbalance between the water supply and demand due to urbanization and industrialization has affected both the quantity and quality of water resources in many parts of the world. Alluvial regions, which harbor productive aquifers, are highly affected worldwide (Postma et al. 1991; Helena et al. 2000; Singh et al. 2006; Singh et al. 2013; Seikh et al. 2017) by these activities. Due to high permeability and porosity, these regions are very susceptible to contamination. Hydrochemistry of alluvial aquifers depends on recharging water, soil–rock–water interactions, impact of neighboring aquifers of surface water, interaction with bed-rock as well as various land use practices (Stallard and Edmond 1983; Datta et al. 2006; Rina et al. 2012). Moreover, from last few decades, change in precipitation pattern which has an impact on recharge, along with this various land use practices and anthropogenic activities such as use of cash crop with high water demand, industrial activities, increasing population pressure has altered these precious resources to such an extent that the use of groundwater becomes limited.

One such region is the alluvial aquifer system of the Indo-Gangetic plain of north-western India,

the most productive region and considered as granary of India. Abundant water resources and highly fertile soil has led to increased food grain production fourfold from 50 million tons in 1950 to 203 million tons in 1999–2000 during green revolution in this region (Joshi et al. 2018). Due to more water requirement by these high yielding crops, a large-scale groundwater depletion has been observed in north-western India. Grace satellite data which works on gravity measurements also suggested that groundwater levels declined at 3.1 ± 0.1 cm per year between 2005 and 2010 (Long et al. 2016; Rodell et al. 2009). The tube well density in this region is >15 per km^2 (Ambast et al. 2006). Haryana state, lying in the Indo-Gangetic Plains (IGP), is a part of NCR (National Capital Region Delhi). Although the state has become self-sufficient in food grain after green revolution but is facing a decline in groundwater table in many parts. The magnitude of the water table declines in the northern and north-western parts of the state ranges from 20 – 30 mbgl in last three decades. During green revolution, a large network of irrigation canals has also been established which has subsequently led to elevation of water table in many parts of the state (Lorenzen et al. 2012). Various authors have reported about secondary salinization and poor quality of groundwater in Indo-Gangetic Plain including Haryana, due to water logging and over irrigation (Tyagi 1988; Datta and de Jong 2002; Meenakshi et al. 2004; Singh 2005; Lorenzen et al. 2012; Sheikh et al. 2017).

The present study has been carried out in Jhajjar district of Haryana, situated in south-western part of NCT Delhi. Jhajjar district is known as a potential freshwater recharge zone in Haryana state, however, in past decades the groundwater is known to have been getting gradually affected by fluoride, sulfate, chloride, salinity, etc. Various authors have reported about poor quality of groundwater in the district as well as its impact: Fluoride contamination in groundwater and dental fluorosis (Yadav et al. 2009), drinking water quality and its health implications (Gupta and Misra 2016, 2018), relationship between water, urine and serum fluoride and fluorosis in school children (Kumar et al. 2017; Haritash et al. 2018). Due to absence of surface water bodies in the district, groundwater is sole source of water for drinking, industrial and irrigation purposes. The stage of ground water development in the district ranges between 77% (block-Beri) to 113% (block-Jhajjar). So, the present study aims to evaluate the subsurface process affecting groundwater resources in the area. Jhajjar is a neighboring district of NCT Delhi, any change in these surrounding areas will also affect the Delhi water situation due to subsurface connectivity, which is already in grim condition.

In last few decades, isotope tracers have been used as a powerful tool for understanding meteorological and hydrological processes. Among available various tracers, stable isotopes of oxygen ($\delta^{18}O$) and hydrogen (δD) are the most important because these isotopes form integral parts of a water molecule. As H_2O molecules travel through various phases of hydrological cycle, they are differentially partitioned (fractionated) and imparting distinguishable isotopic signature in all the three phases. They are conservative in mixing and hence these are used to understand various hydrological processes including groundwater–surface water interaction and contribution of different component on surface flow, recharge characteristics as well as to estimate the mean residence time of water in catchments (Datta et al.1996; Gupta and Deshpande 2005; Jeelani et al. 2010; Maurya et al, 2010, McGuire et al. 2005; Rodgers et al. 2005a). When combined with other measurements (e.g. chloride, EC, temperature, etc.), stable isotopes of water ($\delta^{18}O$ and δD) can be useful indicators of hydrogeochemical processes in the area (Datta et al.1997; Maurya et al, 2010; Rina et al, 2013; Maurya et al, 2019).

In the present study, hydrochemistry along with stable isotopes $\delta^{18}O$ and δD in GIS environment have been used to understand their spatial distribution, geochemical process such as salinity, mixing processes, fluoride enrichment affecting the groundwater quality in the Jhajjar District of Haryana.

2. The Study Area

2.1 Physiography and Climate

The study area Jhajjar District which lie in the path of Indo-Gangetic Plain, extends between 28^{o}

22’ to 28^{o} 49’ north latitudes and 76^{o} 18’ to 76^{o} 59’ east longitudes and covers a geographical area of 1834 sq.km. There are 262 villages in the district and is divided administratively into five blocks: Jhajjar, Bahadurgarh, Beri, Matanhail, and Sahalawas. Physiographically, the district is blanketed with alluvial plain with very small isolated hill in south western part. The alluvial deposits in the district are of Pleistocene to recent in age, with sediments of the district comprised of clay, sand and kankar (carbonate concretion) in varying proportion. The soil contains massive beds of pale reddish brown coloured clay in the southern eastern parts of the area. The carbonate deposits and saltpetre encrustations has been observed in the district (CGWB, 2013).

The climate of the district is semi-arid and hot, except during monsoon months. The cold weather season prevails from January to the beginning of March and followed by the hot summer season which prevails upto the last week of June. The annual rainfall in the district is 532mm. The mean temperature shows a wide range of fluctuation throughout the year with a maximum temperature of 46°C in summer (May–June) and a minimum temperature of 3°C in winter. The monthly mean evaporation exceeds the rainfall amount for all the months except July and August.

Agricultural Practices

After green revolution, in most part of Haryana, irrigation is done by the warabandi irrigation system, which allows the owner of a certain plot to use the entire watercourse or field channel flow for a fixed duration of time proportional to the plot size (Kamra et al. 2002). In Jhajjar districts also 49% area is irrigated by canal water by the warabandi system and 18% area is irrigated by tubewell. Cropping intensity in the district is estimated to 169%, with the two principle types of crop - kharif (monsoon) and rabi (winter). Rice, wheat, millets, sorghum, sugarcane, mustard, pulses, vegetables and fruits are other cash crops in the district (CGWB, 2013).

2.2 Hydrogeology

Alluvium is major groundwater reservoir of the district with a permeable granular zone comprising of sand and gravel with a limited lateral as well as vertical extent. The groundwater occurs in both confined to semiconfined aquifers, but the principle groundwater pool is in granular zones, interbedded with clay in alluvial formation (CGWB 2013).

The various sources of groundwater recharge include rainfall, seepage from canal and irrigation return seepage as well as subsurface inflow whereas the natural source of discharge is subsurface outflow and evapotranspiration(CGWB 2013). The soil texture in the command is mainly sandy loam to fine loam with clay content between 11–17%. The hydraulic conductivity of the unconfined aquifer ranges between 4.7–11.2 m/d with specific yield varies from 0.09 to 0.23 and soil porosity varies between 43.7–53.2%.

The water level depth varies from 0.84 to 12.27 mbgl during pre-monsoon period and 0.21 to 11.90m bgl during post monsoon period. Although the record suggests an overall depletion of 0.005m per year but decadal water level change suggest rise in water level at the rate of about 0.004 to 0.49 m per year (CGWB 2013).This rise in water table (excess of recharge over discharge due to canal network) over a period of time has created twin problem of water logging and salinity in the district which is ultimately leading to loss in soil fertility.

Besides this, huge population of the study area is chronically exposed to higher levels of fluoride from drinking water. The high fluoride concentration has been reported in aquifers, thus making the water undesirable quality for human consumption.

3. Sampling And Analytical Procedures

An extensive field work was carried out using topographic map, a Garmin GPS and satellite image. The sampling locations were selected on 10*10 km grid on ArcGIS platform, so that samples should be collected from uniform distance. Total twenty-one groundwater samples were collected during January 2013 through hand pumps, bore wells and tube wells to assess the groundwater quality. The wells were purged for 5 minutes to avoid mixing of stagnant water in the iron pipes of the wells. Before sampling, the polypropylene bottles were soaked in hydrochloric acid (HCl) for 24 hours and washed with double distilled water and dried. At each site (twenty-one site), water samples bottles were rinsed two or three times with groundwater to be sampled to avoid any contamination. To stabilize trace metals and cations, samples were acidified with ultra- pure HNO_3. Sampling locations of the investigated area is shown in Fig.1.

Analysis of samples were done using standard protocols of American Public Health Association Guidelines (APHA 2012) manual. Few parameters like pH, EC, TDS were analyzed onsite by using their respective electrodes (Hanna make) and depth of water table were also noted. The sampled groundwater was kept in ice containing box made up of Styrofoam and stored at 4° C for further analysis. For the carbonate and bicarbonate determination samples were vacuum filtered with 0.22-micron filter paper. Anions like fluoride (F^-), sulphate (SO_4^{2-}), nitrate (NO_3^-) were measured using ion chromatography (ICS-5000 Dionex). Cation analysis was done using atomic absorption spectrophotometer (Thermofisher, M series). The spatial analysis was done using ArcGIS 10.3.

The saturation index of minerals in groundwater was calculated with PHREEQC software (Parkhurst and Appelo, 1999) through the following expression-

$$SI = \log \frac{IAP}{K}$$

where the dissociated chemical species in the solution are expressed as IAP (Ion Activity Product) and K is the equilibrium solubility product. SI>0 indicates the oversaturation of the minerals in the aquifer that means no further dissolution, while SI<0 indicates the undersaturation of mineral taken, either the groundwater contains insufficient amount of mineral or the short residence time of groundwater in aquifer (Rina et al. 2011)

3.1 Isotopic analysis

A sealed aliquot of samples was used for analysis of stable isotope composition; oxygen and hydrogen isotopes were analyzed by mass spectrometry using gas equilibration method (Epstein and Mayeda. 1953) at Nuclear Hydrology Laboratory, NIH Roorkee. Isotopic analysis was done using the standardized method of equilibrium with CO_2 and H_2 in isotope ratio mass spectrometer.

For oxygen isotope composition, 1mL of water sample was equilibrated with CO_2 and H_2 and the equilibrated gas was introduced into the spectrometer. The reproducibility of the measurement was better than 0.1‰ for $\delta^{18}O$ and 1‰ for δD. The stable isotope results are reported using conventional delta (δ) notation (Craig. 1961). The values of $\delta^{18}O$ and δD obtained in laboratory are corrected using an integrated calibration curve based on VSMOW2 measurements. The δ values are calculated by

$$(‰) = (R_{Sample}/R_{standard} - 1)1000$$

where R denotes the ratio of heavy to light isotopes (e.g. $^{18}O/^{16}O$ or D/H). The values of δD and $\delta^{18}O$ are normally reported relative to SMOW (Craig. 1961) or the equivalent Vienna-SMOW (VSMOW) (Gonfiantini, 1978).

Deuterium excess was calculated for individual pairs of $\delta^{18}O$ and δD in a dataset. *d-excess* value represents the fractionation between oxygen and hydrogen isotopes, and it is defined as: *d excess* (‰) = $\delta^2H - 8*\delta^{18}O$ (Dansgaard. 1964). The *d-excess* signifies the isotopic signature of evaporation under non-equilibrium (kinetic) conditions and the rapid recycling of the vapour. The *d-excess* values of precipitation can provide insight to sources of moisture, atmospheric processes, and relative humidity (Merlivat and Jouzel. 1979). In dry climatic conditions, during evaporation, $d^{18}O$ is more fractionated compared to d^2H, so the liquid phase is relatively more enriched in $d^{18}O$ compared to d^2H. Consequently, the resultant vapour is relatively more enriched in d ^2H compared to $d^{18}O$, due to kinetic effects. This will lead to decreased *d-excess* of isotope imprints in water and consequently the *d*-excess of resultant vapour correspondingly increases (Clark and Fritz. 1997; Kendall and McDonnell. 1998; Gupta and Deshpande. 2005).

3.2 HCA and hydro-chemical analysis

In the analyzed hydrochemical data Chemometric analysis was performed using Cluster analysis which is widely used classification method in water resource management(Singh et al, 2012; Singh et al, 2012; Maurya et al, 2019; Nogueira et al. 2019). This classification technique groups the hydrochemical data into cluster or water type which are interpreted in relation to hydrogeological, climate and land use characteristic of that region. The obtained similar cluster or water group further helps in interpretation of scatter plots with relevant physicochemical parameters. This approach is very helpful in future sampling strategy in an optimal manner in the water quality assessment and monitoring program, which reduces the time and cost of sampling.

Before clustering hydrochemical data was normalized using Z-transformation to ensure data normality, changing the weights of different species or variables and removing the effect of measurement units (Thyne et al. 2004; Singh et al. 2012). Standardization tends to increase the influence of those variables whose variance is small and reduce the influence of variables whose variance is large. HCA was performed on the normalized data set by means of Ward's method using squared Euclidean distances as a measure of similarity.

4. Results And Interpretation Of Field Data

4.1 Hydro-chemical characteristics and spatial distribution of data

The results from the physico-chemical and isotopes analysis of groundwater is given in Table 1, with statistical parameters maximum, minimum average and standard deviation. All samples have ionic balances less than 5%.

The observed pH in analyzed groundwater samples ranged from 7.52 to 10.31 with the average value of 8.4, which suggests the alkaline nature of the groundwater in the area. Few areas like Chhucchakwas, Dubaldhan, Matanhail and Badli, which are present on (North western) part are highly affected with the increased pH in the groundwater (Fig. 2a) which is above the permissible limit by WHO guidelines of safe drinking of water quality (6.5-8.5). In the analyzed groundwater samples, EC ranged from 700-18430µS/cm with the average of 4179.5µS/cm. Spatial variation of EC and TDS is shown in (Fig.2b and 2c). TDS in the observed samples ranged from 351-9215mg/L with a mean value of 2084.5mg/L, 95% samples of groundwater are above the permissible limit of drinking purpose (<500mg/L) as suggested by WHO. TDS concentration from 0-1000mg/L is categorized as fresh water for drinking and agricultural activity, 1000-10000mg/L as saline and greater than 10000 is considered as brackish water. The study area like Chhuchhakwas, Dadri Toye, Majra Asanda, Dubaldhan, Dulhera and Badli water is saline as shown in spatial variation (Fig. 2c). 57% samples are above the permissible limit of drinking water quality. Deposition of salt encrustation due to evaporation in stagnant water (small ditches and ponds) as well as irrigation return flow increases the total salt concentration which is contributing to high EC and TDS of the study area (Lorenzen et al. 2012).

Hydrochemistry

The relative abundance of the major cations and major anions of analyzed groundwater were in

the following order: $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ and of $Cl^- > SO_4^{2-} > HCO_3^- > NO_3^- > F^-$. The concentration of major cations such as sodium, calcium and magnesium contribute to 98% of the total cations present in the groundwater samples.

The most dominant anion Cl^- varied from 32.1-2851.4mg/L with an average value 711.1mg/L. At 65% of sampling sites, chloride in groundwater in more than permissible limit of WHO. Spatial variation of chloride (Fig.3b) suggests that only in eastern part of the area as well as south eastern part less chloride concentration was observed, whereas in other parts high chloride concentration was observed. The area is underlain by alluvial deposits of quaternary system represented by Pleistocene and recent sediment. Geographical conditions (Flat alluvial plain) and regional semi- arid climate favours the evaporation. Before recharge, evapotranspiration from open water bodies, namely, reservoirs, irrigation canals as well as irrigation return flow, amplifies the total salt concentration (Misra and Mishra 2007; Stigter et al. 1998). After Green revolution, construction of the canal network to fulfill the water demand and subsequent rise in water table, are major source of salinization in the Indo-Gangetic plain. It leaches the stored salt from the unsaturated zone as well as dry-fall out (wind-blown dust containing salt from Aravali Deserts) is also imparting high chloride concentration in the Delhi and surrounding area (Datta et al. 1997; Lorenzen et al. 2012).

The concentration of SO_4^{2-} in the groundwater ranges from 23.3 to 1851.4mg/L. Besides dissolution of sulphate minerals such as gypsum and anhydrite, high sulphate concentration from agrichemicals (leachable sulphates present in fertilizer), breaking of organic substances from top soil/water and other human influences (Craig and Anderson 1979) is imparting high sulphate in the study area. Except at south western and eastern part, in the whole study area high sulphate concentration was observed. Spatial variation of sulphate map is given in Fig.3d

The third largest contributor of anion is bicarbonate, ranges from 122 to 394 mg/L with average value of 244.1 mg/L. Dissolution of carbonates and reaction of silicates with carbonic acid account for the addition of HCO_3 to the groundwater. The study area is a part of Indo-Gangetic alluvial plain, where abundant primary and secondary calcite minerals like clay, kankar are present in upper parts of earth, will also favour dissolution of high bicarbonate concentration in the aquifer of the area, as shown in the reaction.

$$CaCO_3 + CO_2(g) + H_2O = Ca^{2+} + HCO_3^-$$

$$CO_2 + H_2O = H + HCO_3$$

The maximum bicarbonate concentration was observed in north-western part in the study area,such as Chhuchhakwas, Sunderheti and Amadalpur etc.

Nitrate contamination in aquifers

The nitrate concentration in observed samples varied from 10.2 to 54.3mg/L with its average value of 34mg/L. From the spatial variation map (Fig.3c) it can be inferred that south eastern and southwestern part of the study area, Mundahera, Dadri Toye, Dulhera and Hassanpur are mainly affected with high nitrate concentration in groundwater in groundwater. At all the sampling locations nitrate concentration in groundwater was more than 10mg/L, whereas at approximately 30% of the location nitrate concentration in groundwater is more than 45mg/L (maximum permissible limit by WHO). Due to absence of any geological deposits, nitrate concentration can be attributed to anthropogenic activities such as the excessive use of ammonical fertilizers for crops, excessive water, agricultural return flow and various point sources which contribute to the NO_3 in groundwater (Rina et al, 2014).

$$NH_4 + 2O_2 = NO_3 + 2H + H_2O$$

Direct recharge, water input from irrigation and evapotranspiration which amplifies this, is the main physical processes that influence nitrate concentration (Debernardi et al. 2008). Various biogeochemical processes, especially plant uptake, microbial processes and other various transformation processes such as denitrification, as well as water table depth are other factors, which plays an important role (Datta et al. 1997; Rina et al. 2012).

Fluoride Toxicity

Sever fluoride toxicity has been reported by various authors (Yadav et al. 2009; Gupta and Misra 2016) in the district. In the observed groundwater samples, fluoride concentration ranged from 0.6 to 6.8mg/L with the average of 2.6mg/L. From Spatial variation of fluoride distribution (Fig.3a) it can be inferred that north eastern and central region (Bahadurgarh and Barahi areas) of the study area is highly affected by the fluoride concentration. Approximately 66% of sampling location has exceeded the WHO (1.5mg/L) and 71% of samples from BIS (2012) permissible limit (1.0mg/L) of drinking water quality parameter. Alkaline pH in aquifers, high evapotranspiration due to semi-arid climate, ion exchange processes in the host bed-rock between fluoride and hydroxyl ions (mica and amphiboles) is escalating fluoride enrichment in groundwater. Besides that, long residence time and changes in facies during ion-exchange of groundwater flow regime is also augmenting fluoride concentration in groundwater (Raj and Shaji 2017). The study area is a part of Indo-Gangetic alluvial plains, which are dominated by clay-silt, clay and grey micaceous sand formations. Clays rich in fluoride containing minerals and their weathering increases fluoride concentration in aquifers. Further, granitic rocks also play a major role in enrichment of the fluoride concentration in groundwater owing to the dissolution of minerals (Singh et al. 2012). In most of sampling locations HCO_3^-/Ca^{2+}ratio, was also greater than one, which favors the geochemical conditions for the fluoride dissolution processes (Saxena and Ahmed 2003) in the aquifer materials. Also, at most of locations Na^+/Ca^{2+} is greater than one, suggesting low calcium activity and high sodium, high sodium leads to fluoride dissolution from fluoride bearing minerals at higher pH (Singh et al. 2012).

Correlation of Physico-chemical Parameters

Correlation (Pearson) is a bivariate analysis to identify degree of dependencies between variables. pH shows strong correlation with EC, TDS, Na^+ and Cl^-. A good correlation in EC and TDS in samples were present which suggests as conductivity increases as the concentration of all dissolved constituents/ions increases. The correlation matrix of physicochemical parameter of groundwater samples is shown in table 2. The good correlation was seen between Na^+ and Ca^{2+}, Na^+ and Mg^{2+}, Ca^{2+} and Mg^{2+}, Na^+ and Cl^-, Ca^{2+} and Cl^-, Mg^{2+} and Cl^-, Na^+ and SO_4^{2-}, Mg^{2+} and SO_4^{2-}, Ca^{2+} and SO_4^{2-} indicates similar origin. High correlation between Na^+ and Cl^-(r^2=0.95) indicates halite dissolution in the area. Good correlation between Cl^--NO_3^-, Cl-SO_4^-, K-NO_3^-, Mg-NO_3^- and NO_3^--SO_4^{2-} suggests possible impact of leaching of excess fertilizers used for agricultural activity, that may create a long-term risk of groundwater pollution and salinity also. The positive correlation between Ca and SO_4 suggests the similar origin, besides dissolution of anhydrite in aquifer matrix, gypsum application in fertilization could be sources.

Mineral Saturation Index of the study area

The Saturation Index (SI) is the ratio of the apparent ionic product to the apparent solubility product of the given minerals. SI values of different minerals present in the geological formation of the area is given in the Fig.4. Groundwater is undersaturated with respect to anhydrite, gypsum and fluorite at most of the sampling locations, suggesting significant contribution of SO_4^{2-} and F^- ions to the groundwater by dissolution of these minerals. Oversaturation of calcite, dolomite and aragonite shows that these minerals have already precipitated and are leading to enrichment of Ca^{2+} and Mg^{2+} in the groundwater. Oversaturation can be possibly produced by factors that include incongruent dissolution, common ion effect and evaporation (Rina et al, 2012). As a result of irrigation, groundwater was originally saturated with respect to calcite, ET causes an increase in concentration of Ca due to supersaturation followed by precipitation of calcite (McCarthy and Ellery, 1994; Stigter et al. 1998) due to semi-arid condition. Undersaturation of gypsum and anhydrite and various anthropogenic activities are the possible source of sulphate. Except at the few locations, Fluorite is undersaturated at most of the sampling locations. Alkaline environment in the sub-surface and oversaturation of calcium may lead to release of fluoride at these locations.

Water sample grouping (HCA) and type

Physico-chemical characteristics of different water group-

Hierarchical cluster analysis (HCA) resulted in three main water groups, namely-WG-1, WG-2, WG-3. WG-1 encompasses a total of 14 samples, these samples represent freshwaters with the lowest EC values (less than 5000µS/cm) and Cl^- concentrations (500-1000 mg/l). Na/Cl ratio is either very low or very high.

WG-2 represents 6 sampling location where electrical conductivity varied between 5000-10000µS/cm and Cl^- concentration varied from 1000-2500 mg/L. Sampling locations in WG 2 are mostly located in urban part of the district such as in Bahadurgarh and Jhajjar block. Groundwater level in these blocks are 6-9 and >9 mbgl, also, these are the areas where maximum decadal change in water level has been observed (Fig.9a). Na/Cl at these locations is low (<0.8) suggests deep saline upconing of groundwater. WG3 is represented by one sampling well with singular characteristics, therefore, being in a separate group with 18430µS/cm. Na/Cl ratio at this location is high (1.01), showing highly saline water similar to seawater.

Stable isotopes ($\delta^{18}O$ and δD) investigations

In isotopic signature from analyzed groundwater samples of the area, varied from $\delta^{18}O$ =

[-9.49‰ to -4.70‰] with average $d^{18}O$=-6.86‰ and SD=1.41‰ and δD= [-63.83‰ to -35.79‰] with an average -49.03‰ and SD=7.24‰ has been observed. Depleted isotopic composition is observed in small pocket of northern and most of the peri-urban area. Most enriched value was observed in central urban region i.e in Jhajjar block.

Deuterium excess

d-excess of the study area ranged from [-0.30 to 12.10‰] with average value 4.40‰. The average *d*-excess of meteoric waters is ~10‰. Deuterium excess (*d* -excess) is a important tool to investigate the contribution of water vapour from different sources at a specific location (Gupta and Deshpande 2005), as well as secondary processes such as evaporation and freezing effects during rain events and recirculation of moisture from large inland water bodies (Gupta and Deshpande 2005, Geelani et al, 2015). The signature of *d*-excess in groundwater decreases when it undergoes kinetic evaporation in the vadose zone, mixing of waters from different origins. At most of sampling locations in the study area *d-excess* is less than 10, which signifies that at these locations significant evaporation has taken place before recharge. In north eastern and south western part (periurban) where mostly canal irrigation is present, high *d-excess* is present suggesting more influx of water in those area, Spatial variation of oxygen and *d-excess* isotope in groundwater samples of the Jhajjar district is shown in Fig.6a & b.

$d^{18}O$-dD regression lines

Due to absence of isotopic signature of precipitation data of the study area, it has been compared with equation of LMWL of Delhi area (Gupta and Deshpande 2005), given in equation below:

New Delhi $\delta D = (7.2 \pm 0.1)* \delta^{18}O + (4.6 \pm 0.5)$ [$R^2 = 0.95$] (Source: GNIP)

The $\delta^{18}O$ and δD regression line of analyzed groundwater samples of the study area [$\delta D = (5.03 \pm 0.23)* \delta^{18}O - (14.49 \pm 1.61)$] is below the LMWL of Delhi. Also the similar isotopic signature has been observed in groundwater samples of Delhi region (Das et al. 1988; Datta et al. 1996) and in Sonipat Region, (Seikh et al. 2017). Lower regression line of $\delta^{18}O$ and δD of groundwater samples (Fig.7a) from the local meteoric waterline line (LMWL) of neighbouring station suggests non-equilibrium kinetic fractionation during evaporation.

5. Discussion

5.1 Origin of water

From the scatter plots of $d^{18}O$ and dD (Fig.7a) it can be inferred that all the sampling locations are around the regression line which suggest recharge of groundwater in the area is predominantly from inheritance of local precipitation. Groundwater regression line ($d^{18}O$–dD) slope (5.03) is significantly lower than that of the LMWL (7.2), indicates a combined effect of local atmospheric and ground surface processes before recharge and it suggests a minor to significant evaporation of water before recharge in the area (Gupta and Deshpande 2005).

A wide spatial variation in $d^{18}O$ (Fig.6a) can be attributed to land use activities in the area. Depleted isotopic composition has been observed only in one patch in central part and most of the peri-urban area. Due to continuous influx of water through canal irrigation depleted isotopic composition has been observed in these parts of the study area. Enriched isotopic composition has been observed at south western part (Mantanhail and Sahlawas) block and south eastern part of the study area and the most part of central region.

The annual mean isotopic composition of precipitation in Delhi (d^{18}O=-5.4%, dD=-35%) has been reported (IAEA/WMO,2009), but during late monsoon (August-September) isotopic composition d^{18}O=-6.8‰ to -8.6‰; and dD=-46‰ to-58‰ has been observed (Datta et al. 1991), and late monsoon is contributing 80% of the total annual precipitation (CGWB-GOI, 2006) in this area. The observed average isotopic composition d^{18}O=-6.86‰ in the study area suggests late monsoon recharge. It has been reported that in Haryana region, rainfall contributes only 15% recharge (Goel et al. 1977), besides this irrigation by canals system are the major potential source of recharge in the area. Due to continuous influx of water through canal irrigation depleted isotopic composition has been observed in the peri-urban part of the area, suggesting an important source of recharge.

Also, various post -precipitation processes such as selection, mixing and evapotranspiration from and within the vadose zone also significantly changes isotopic composition of precipitation before groundwater recharge (Gupta and Deshpande 2005).

2. *d-excess* versus d^{18}O (Fig.7b) suggests, depleted isotopic composition has higher *d-excess,* whereas enriched isotopic composition has lower *d-excess.* In urban area, where more depletion of groundwater was coupled with less influx of water is taking place, an enriched d^{18}O and *d-excess* values less than 10‰ has been observed, suggests significant evaporation during recharge.however, in peri-urban area with sufficient influx due to canal irrigation, depleted d^{18}O and *d-excess* values more than 10‰ was observed.

5.2 Groundwater Salinity, Fluoride enrichment and d^{18}O

A scatter plot of Cl versus δ^{18}O (Fig.8a) depicts the relationship between salinity and isotopic composition. The graph suggests that sampling locations with depleted isotopic composition has a lower chloride concentration except for few locations. These sampling locations are mostly found in peri-urban area such as Sahalwas, Matanhail, few regions of Bahadurgarh and Beri block where water level is less than <3 mbgl. In few of these areas increase in water table has been observed during last decade due to canal irrigation. Less water level depth in these areas and sufficient influx of water due to canal irrigation, suggests natural hydraulic equilibrium in these is not disturbed, thus imparting less chloride and depleted isotopic signature in these aquifers. Urban (Central) part of the district, Jhajhar block (Urban part) which is in critical category in terms of groundwater development, is showing maximum depletion in groundwater (Fig.9a). Flat topography (Fig.9b) which led to high evaporation coupled with more depletion of groundwater in these area, enriched d^{18}O and high chloride concentration was observed. From the spatial variation (Fig.3a) of chloride as well as scatter plot of d^{18}O and Cl (Fig.8a) suggests lateral mixing of nearby aquifers. Upconing of deeper saline water and its mixing with shallow groundwater may leads to saline water plumes in shallow aquifers and expansion of lateral extent of pollution and salinity. In Delhi and Haryana, fresh or brackish shallow groundwater is often underlain by saline water (CGWBGOI 2006; Rao et al. 2007), so gradual increases in salinity with depth has been observed. Jhajhar block is most afftected by this and further depletion in water table will affect the adjoining aquifers of Delhi and Gurgaon.

Along with chloride, in north and northwestern part of the study area Matanhail, Beri and Sahalwas block low fluoride concentration has been observed. These are peri-urban part where due to canal irrigation less depletion in groundwater has been observed. Scatter plot (Fig.8b) also suggests that lowest fluoride concentration was observed with depleted isotopic composition (d^{18}O), whereas high fluoride concentration is observed with enriched isotopic composition. The study area is a part of Indo-Gangetic alluvial plains, which are dominated by clay-silt, clay and grey micaceous sand formations. Clay rich formations are rich in fluorine and other salts (Gupta and

Misra 2018) leading to fluoride dissolution in the aquifer matrix. Central part of the study area which are urbanized part such as Jhajjar block as well as in few parts of Bahadurgarh block where maximum depletion in groundwater has been observed in last decades. At these locations, high fluoride concentration coupled with enriched isotopic composition has been found, less flushing of aquifer with freshwater and longer retention time leads to enrichment of fluoride concentration and enriched isotopic composition has been observed at these locations. Groundwater Fluoride concentration at any location is controlled by recharging water through the unsaturated zone and by lateral groundwater flow from the surrounding areas (Datta et al. 1996).

At three sampling locations, JH1 and JH2 and JH15 highest F^- concentration is associated with depleted isotopic composition. JH1 and JH2 sampling location in the north-eastern part of the district which is nearer to Sonepat district, is showing highest fluoride concentration (Fluoride concentration 6.1-6.7mg/L, Seikh et al. 2017), due to subsurface connectivity of aquifer, high fluoride concentration has been at these locations.

Scatter plots (Fig.8a and b) also depicts about lateral mixing process in the nearby aquifers due to depletion in water table. Except at few locations, highest fluoride concentration is being observed at the places with highest salinity. As mentioned earlier in above paragraph, less flushing of aquifer with freshwater and recharge of evaporated water and longer retention in aquifer is leading to fluoride enrichment coupled with high salinity (Sekhar et al. 2006), similar observation was also observed by Gupta et al. 2005 in northern Gujarat where areas of high fluoride overlap areas with high electrical conductivity (EC). Further depletion in water level will increase the fluoride enrichment and salinity.

5.3 Provenance, water–rock interaction and hydrological processes in the area

To study various hydrological processes occurring in the area scatter plots and various ionic ratio has been used. In the scatter diagram Ca^{2+}+Mg^{2+} vs $SO4^{2-}$+$HCO3^-$ (Fig.9a), most of the sampling points present above the equiline, which suggests reverse ion exchange and carbonate weathering is dominant process in the study area, few samples are along the equiline indicate that these ions are released into the aquifer due to weathering of both silicate and carbonate minerals and at only one sampling location, which lie below equiline suggests silicate weathering is imparting ions into the aquifer (Datta et al.1996;Manish et al, 2006, Rina et al. 2011).

Weathering/dissolution processes increases groundwater mineralization during subsurface flow, which is also reflected with the increase in concentration of HCO_3^- along with major cations in pathways. This is either due to high solubility of carbonate minerals (e.g. calcite, dolomite), or due to the slower weathering of silicate minerals such as Ca plagioclase (Nogueira et al. 2019). Water group I (WG I) is representing low EC with low alkalinity which reveals that it is predominantly new water derived from young and local recharge with very little interaction with the aquifer material. During subsurface flow pathways, in groundwater hydrochemistry besides dissolution, ion exchange of cations on clay minerals are a very important process which governs the hydrochemistry. Sodium clay minerals such as montmorillonite which has high capacities for base exchange (Rina et al, 2012; Manish et al,2006), when this sodium clay (montmorillonite) interacts with aquifer solution in which calcium is the predominant ion, it enriches the groundwater with sodium.

Upon cation exchange during subsurface flow, Ca^{2+} on the exchanger complex is replaced by Na^{2+}, as expressed by equation (Appelo and Postma 2005), this leads to the salinization of aquifers

$$2Na^+ + Ca - X \longleftrightarrow 2Na - X + Ca^{2+}$$

where X represents the complex exchanger (aquifer material).

EC and chloride content increase consistently from WG-1 to WG-2 towards WG-3. These two groups are characterized by low Na/Cl ratios (0.5-0.9) and high Ca/HCO_3 ratios (ranging from 1 to 6) which revealed the cation exchange process in the brackish/salt water groups. Na/Cl ratios varied from 0.213 to 1.90 with mean ratio 0.770, in WG1 is showing a very wide and varied Na/Cl ratio either very low or vary high with low chloride concentration, where as in WG2 and WG3 with increase in chloride concentration Na/Cl ratio is decreasing suggesting salinity at these locations is due to wastewater infiltration, few samples of these WG2 is showing similar character of ocean water ratio (0.86-1.0). Hydrochemical relationship of Na/Cl vs Cl is shown in Fig.(9b).

Medium correlation was observed between Ca^{2+} and $SO4^{2+}$, undersaturation of zypsum and anhydrite, as well as in WG2 and WG3 high sulphate concentration in the urban area is more likely related to domestic and industrial activities (Rina et al. 2013, Manish et al, 2006) could be reason of high sources of sulphate. In these groups less gypsum dissolution can also be explained with the high SO_4/Cl^- ratios in brackish water. Hydrochemical relationships of Ca and SO4 is given in Fig.(9C). The study area is a part of Gangetic Plain, where primary and secondary calcite minerals (e.g. detrital carbonate grains, kankar concretions, grain coatings) are reported abundant in the alluvial aquifer (Yadav and Rajamani, 2004), so groundwater is mostly saturated with respect to $CaCO_3$ (Fig.4). Also due to more solubility of $CaSO_4$ than $CaCO_{3,}$ the dissolution of CaSO4 has a direct effect on $CaCO_3$ saturation due to common ion effect. Increasing Ca^{2+}concentrations may even trigger the precipitation of $CaCO_3$ when the ion activity product of Ca^{2+} and $HCO_3{}^-$ exceeds saturation also evaporation led to supersaturation of Ca^{2+} in the system.

Besides multiple sources of ions in groundwater, geographic condition and change in land use/land cover is also playing an important role in groundwater salinity and increasing mineralization trends in the shallow aquifers. Topographically flat Surface in the area (Fig. DEM of study area), flow accumulation map (Fig.9b) also suggests that geography favors the water logging in the area. The evapotranspiration from flat surface as well as from these waterlogged areas and irrigated fields is an increasing concern in the alluvial plains and often directly connected to change in land use activities. Besides this, various authors also reported about in the geologic past, especially during increased arid periods due to weekened of failed monsoon during the last glaciation (Thussu 2004), which has led to built up of salt encrustation in the sediments in the area. Higher salinities in urban area with WG2 and WG3 showing brackish waters samples can be linked to different recharge patterns that is associated with current land use practices which is leading to water excavation in the area.

6. Concluding Remarks

In Delhi and its adjoining areas, water resources are under high stress due to urbanization which leads to overexploitation and pollution. Identifying and determining the aquifer vulnerability is one of the most important steps for maintaining sustainable water resource management. The present study was done in Jhajjar district, a part of Indo-Gangetic alluvial aquifer. Human induced activities such as indiscriminate withdrawal of groundwater, canal irrigation and disposal of waste is leading to serious consequences on environment of the region. Groundwater quality assessment was done using multiple geochemical analysis and stable isotopes ($\delta^{18}O$ and δD) to identify the sources and transformation processes. Based on various chemical parameters, three water group was discerned, the composition of these water groups is influenced by natural and human activities.

In peri-urban part where sufficient influx of water is taking place in aquifer during canal irrigation and less depletion in water table was observed, depleted d^{18}O and less chloride and less fluoride content was observed. Whereas in central part where more depletion was observed than influx, enriched d^{18}O and high chloride and fluoride content was observed. Due to flat topography and semi-arid climatic condition, evapo-transpiration of rain water and irrigation return flow as well as dissolution of calcite, dolomite and gypsum are the main processes that determine processes that determine the the basic composition groundwater in the study area. Also, high Fluoride concentration is attached with Na-Cl hydro-chemical facies. The present study also suggests that salinization of aquifers in the study area is not a homogeneous process but is related to different sources and dynamics. Further depletion in groundwater will favour the salinity as well as fluoride enrichment in the study area. Protection of recharge zones is required to further depletion and contamination of resources. Awareness and education to villagers and water user regarding use, fertilization input only can help this precious resource from further depletion. Along with this regular monitoring and stringent enforcement of law can help the aquifers from further depletion, any change in this area will affect nearby aquifers of surrounding area.

Declarations

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Tables

Table 1.Physico-chemical parameters of Groundwater Samples (all concentration in mg/L, except EC(μS/cm), and pH)

	Min	Max	Avg.	SD	WHO Std.
pH	7.52	10.31	8.4	0.7	6.5-8.5
EC	702	18430	4179.5	4259.2	-
TDS	351	9215	2084.5	2130.1	1000mg/L
Na^+	61.25	1860	447.4	458.4	200mg/L
K^+	1.68	30.84	9.5	6.9	-
Ca^{2+}	26.52	277.18	97.8	74.8	75-200mg/L
Total hardness	208.5	1388.9	690.54	396.7	
Mg^{2+}	31.23	240.16	107.0	58.1	-
$CO3^-$	0	120	29.3	26.9	-
$HCO3^-$	122	394	244.2	77.8	-
F^-	0.6	6.8	2.6	1.9	1.5mg/L
Cl^-	32.1	2851.4	711.1	758.5	250mg/L
SO_4^-	23.3	1851.4	366.0	438.8	400mg/L
NO_3^-	10.2	54.3	34.0	12.2	45mg/L

Table.2 Correlation of Physico-chemical Parameters

pH	*EC*	*TDS*	*Na*	*K*	*Ca*	*Mg*	*CO3*	*HCO3*	*F*	*Cl*	*SO4*	*NO3*	
pH	1.00												
EC	**0.74**	1.00											
TDS	**0.74**	**1.00**	1.00										
Na	**0.72**	**0.99**	**0.99**	1.00									
K	0.42	0.36	0.36	0.36	1.00								
Ca	0.47	**0.87**	**0.87**	**0.85**	0.13	1.00							
Mg	0.48	0.72	0.72	0.72	0.29	0.70	1.00						
CO3	0.31	0.04	0.03	0.03	0.72	-0.22	0.03	1.00					
HCO3	0.26	0.43	0.43	0.43	0.48	0.21	0.29	0.34	1.00				
F	0.04	0.11	0.11	0.11	-0.12	0.18	-0.08	-0.23	**-0.45**	1.00			
Cl	**0.80**	**0.97**	**0.97**	**0.95**	0.32	**0.87**	**0.81**	0.01	0.32	0.09	1.00		
SO4	0.19	0.68	0.68	0.74	0.20	0.70	0.64	-0.20	0.27	0.06	0.61	1.00	
NO3	0.02	0.22	0.22	0.20	-0.05	0.41	0.38	-0.34	-0.22	0.05	0.27	0.34	1.00

Table.3 Chemical Characteristics of different Cluster

WG group	WG-1	WG-2	WG-3
Number of samples	14	6	1
EC (µS/cm)	less than 5000µS/cm	5000-10000 µS/cm	18430µS/cm
Cl^-	500-1000mg/l	1000-2500 mg/l.	2851.4mg/l
Water type (Stuyfzand	fresh	Brackish	Saline
Na/Cl	Very low to very high	<0.8	1.0
$\delta^{18}O$ (‰)	4.70-9.49	4.84-7.6	
Facies	Na-HCO_3, Mg-HCO_3, Mg-Cl, Na-Cl	Na-Cl, Na_2-SO_4	Na-Cl

Table 4. Cluster with similar site characteristics.

Class	1	2	3
Objects	14	6	1
Sum of weights	14	6	1
Within-class variance	925497.670	5177122.479	0.000
Minimum distance to centroid	161.351	441.461	0.000
Average distance to centroid	766.089	1759.998	0.000
Maximum distance to centroid	1818.681	3238.868	0.000
	Sample1	Sample3	Sample8
	Sample2	Sample6	
	Sample4	Sample7	
	Sample5	Sample18	
	Sample9	Sample20	
	Sample10	Sample21	
	Sample11		
	Sample12		
	Sample13		
	Sample14		
	Sample15		
	Sample16		
	Sample17		
	Sample19		

Figures

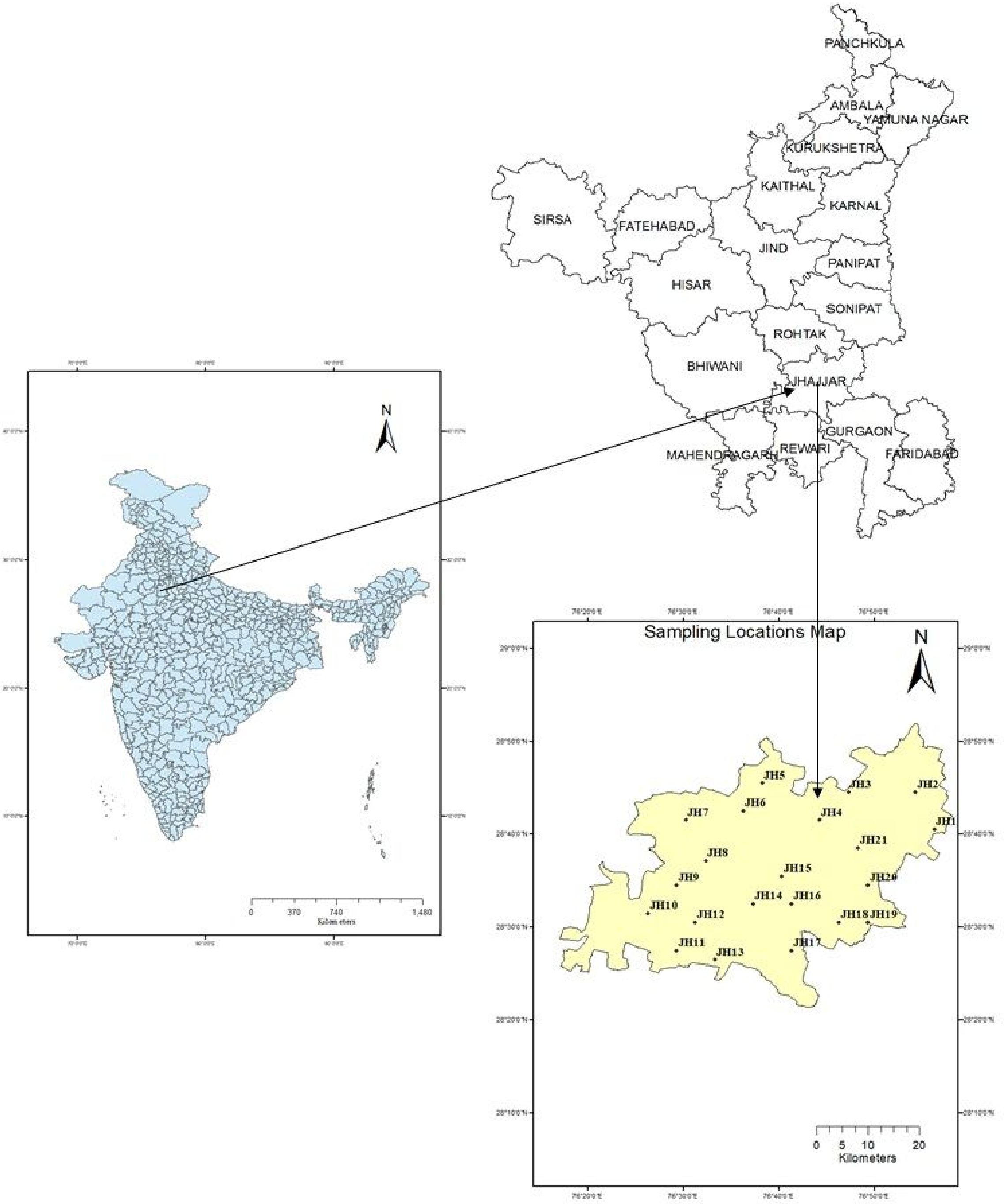

Figure 1

Study Area with sampling locations

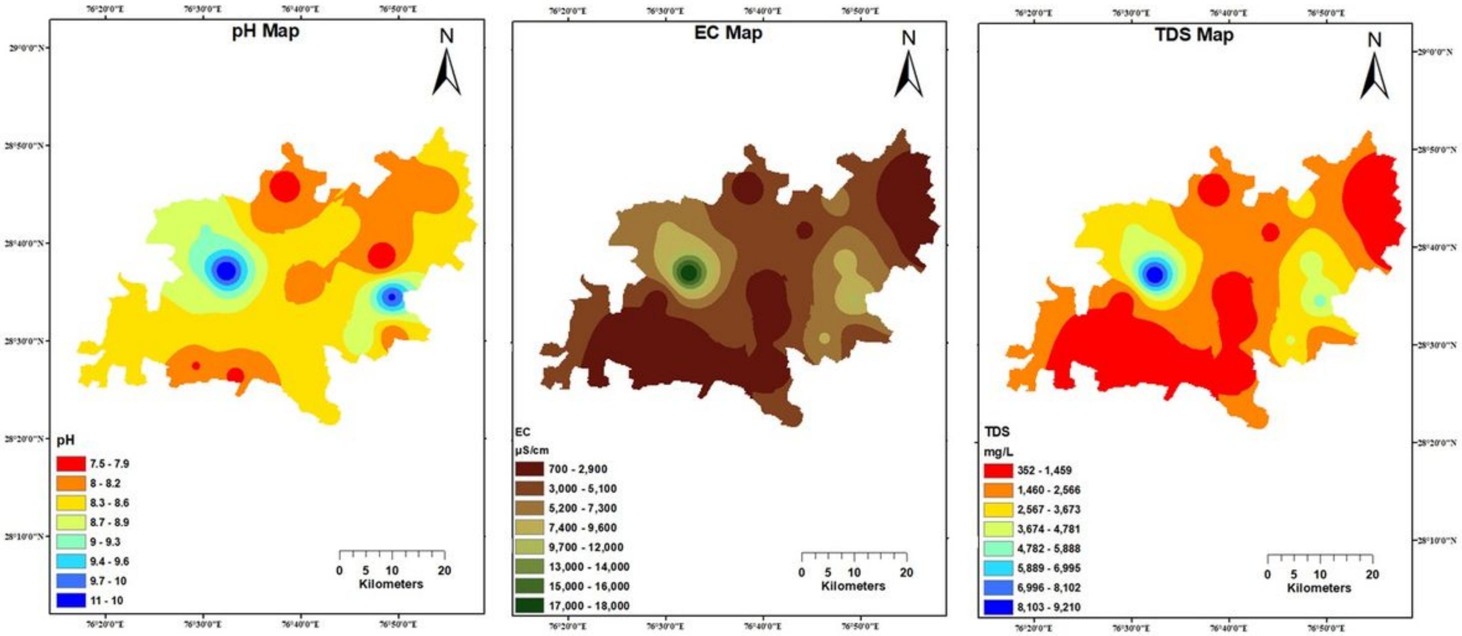

Figure 2

Spatial variation of (a) pH (b) EC and (c) TDS

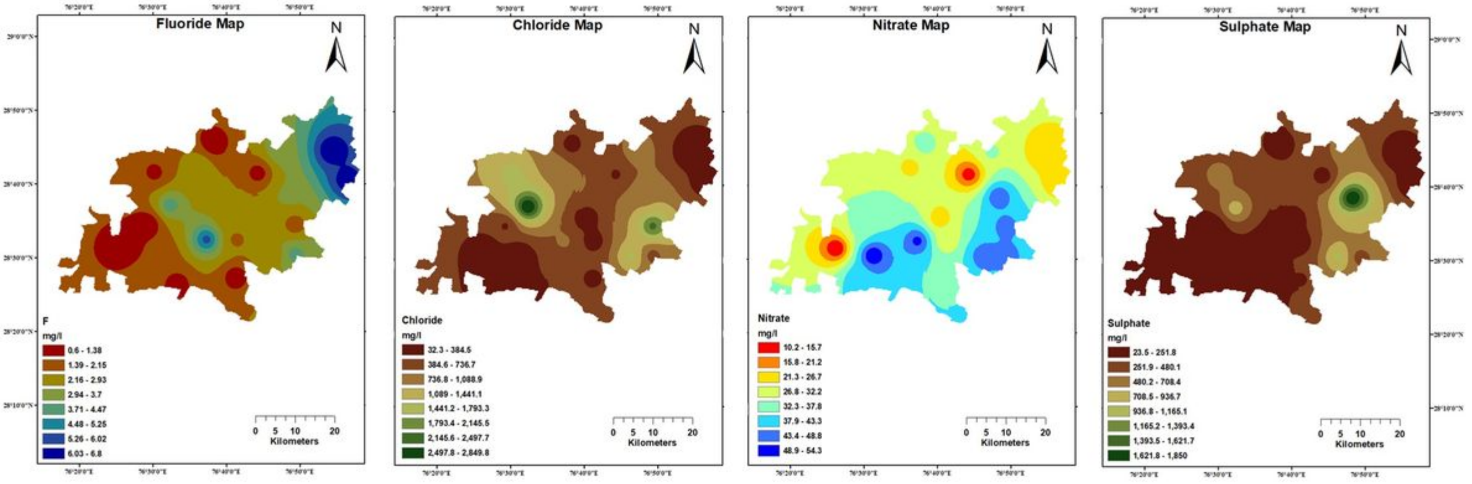

Figure 3

Spatial variation of anions (a) Fluoride (b) Chloride (c) Nitrate (d) Sulphate

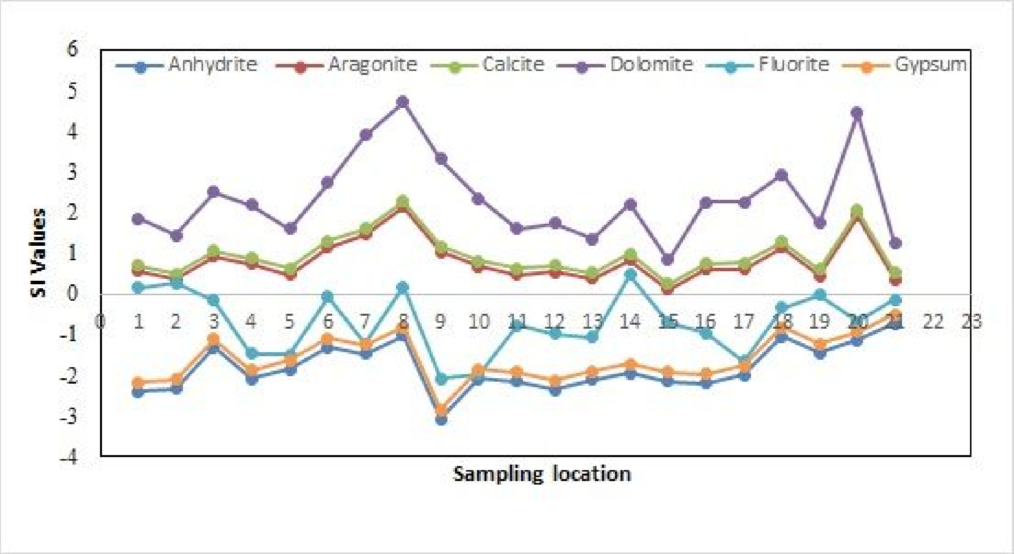

Figure 4

Mineral saturation Index of different sampling locations

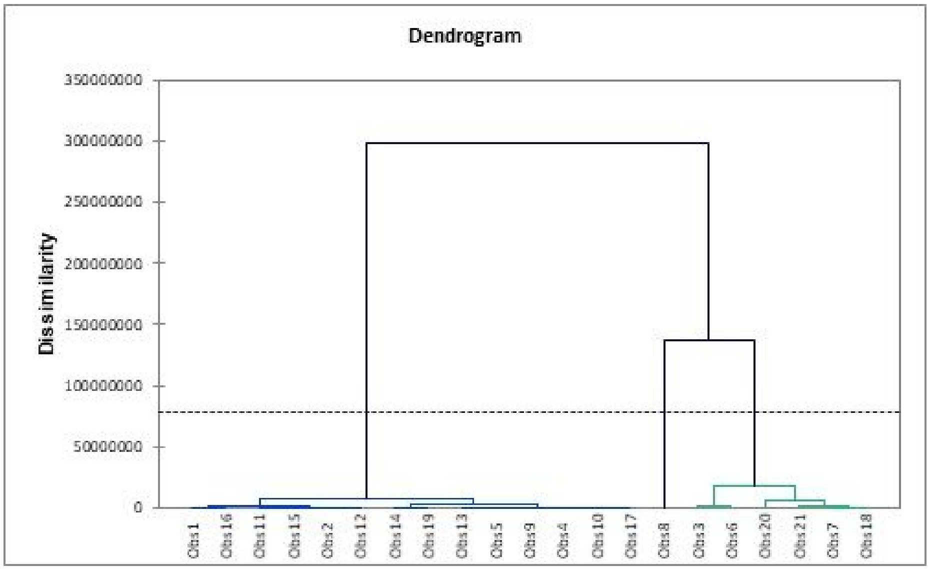

Figure 5

Dendrogram showing clusters of different sampling site

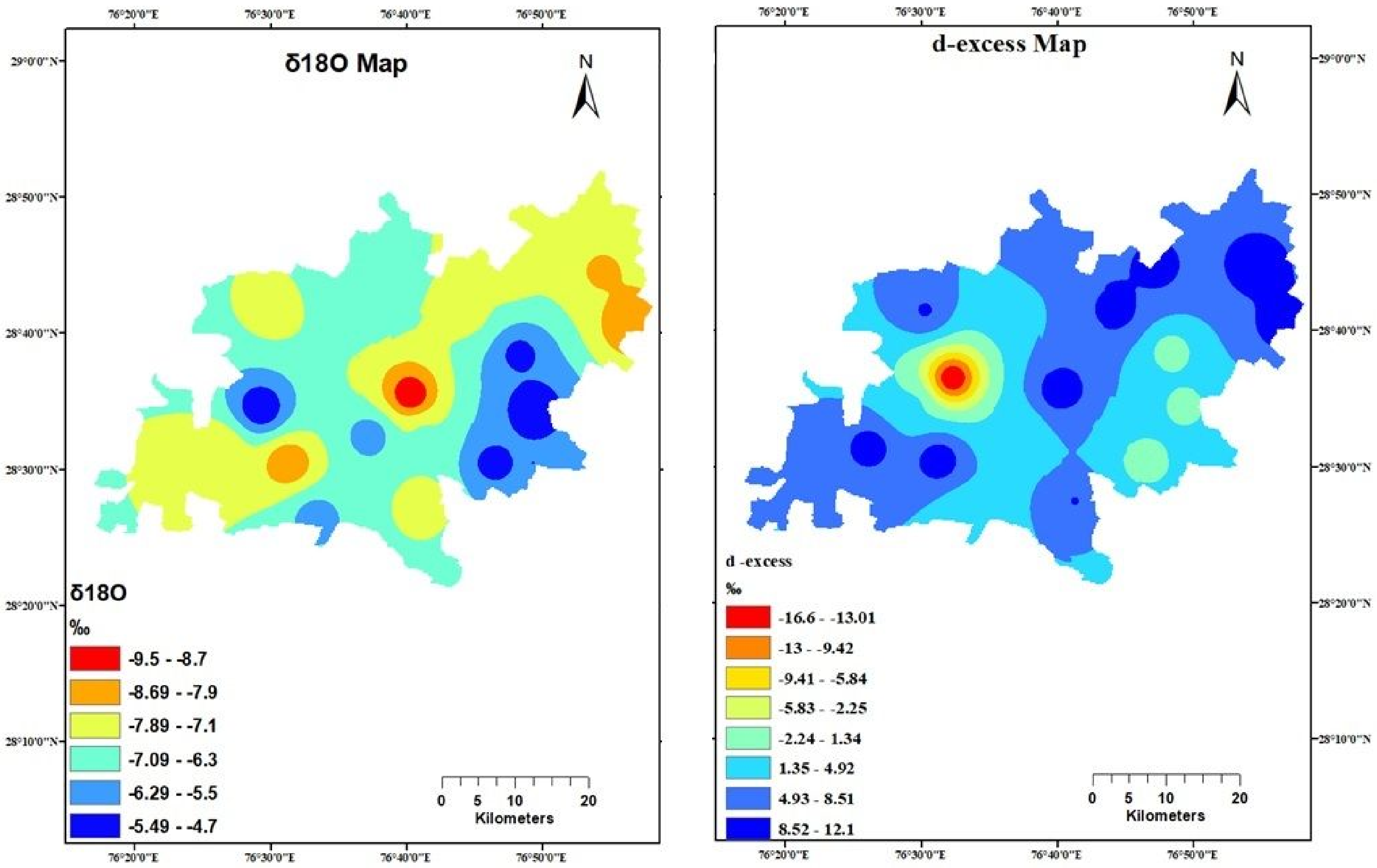

Figure 6

Spatial variation of (a) δ18O and (b) d-excess

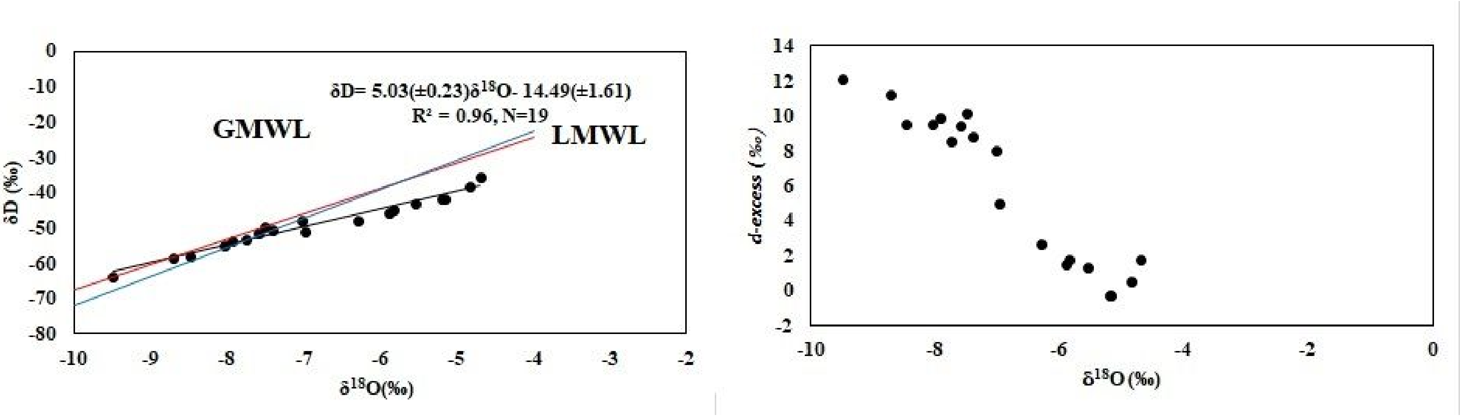

Figure 7

Regression line of (a) δ18O vs δD and (b) d-excess vs δ18O

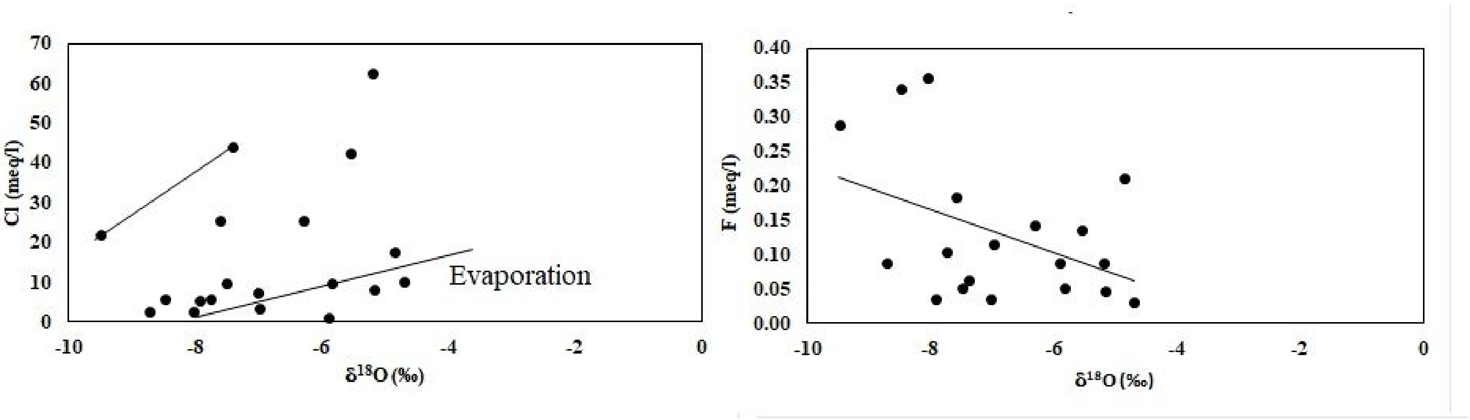

Figure 8

Scatter plots of (a) δ18O vs Cl- (b) δ18O vs F-

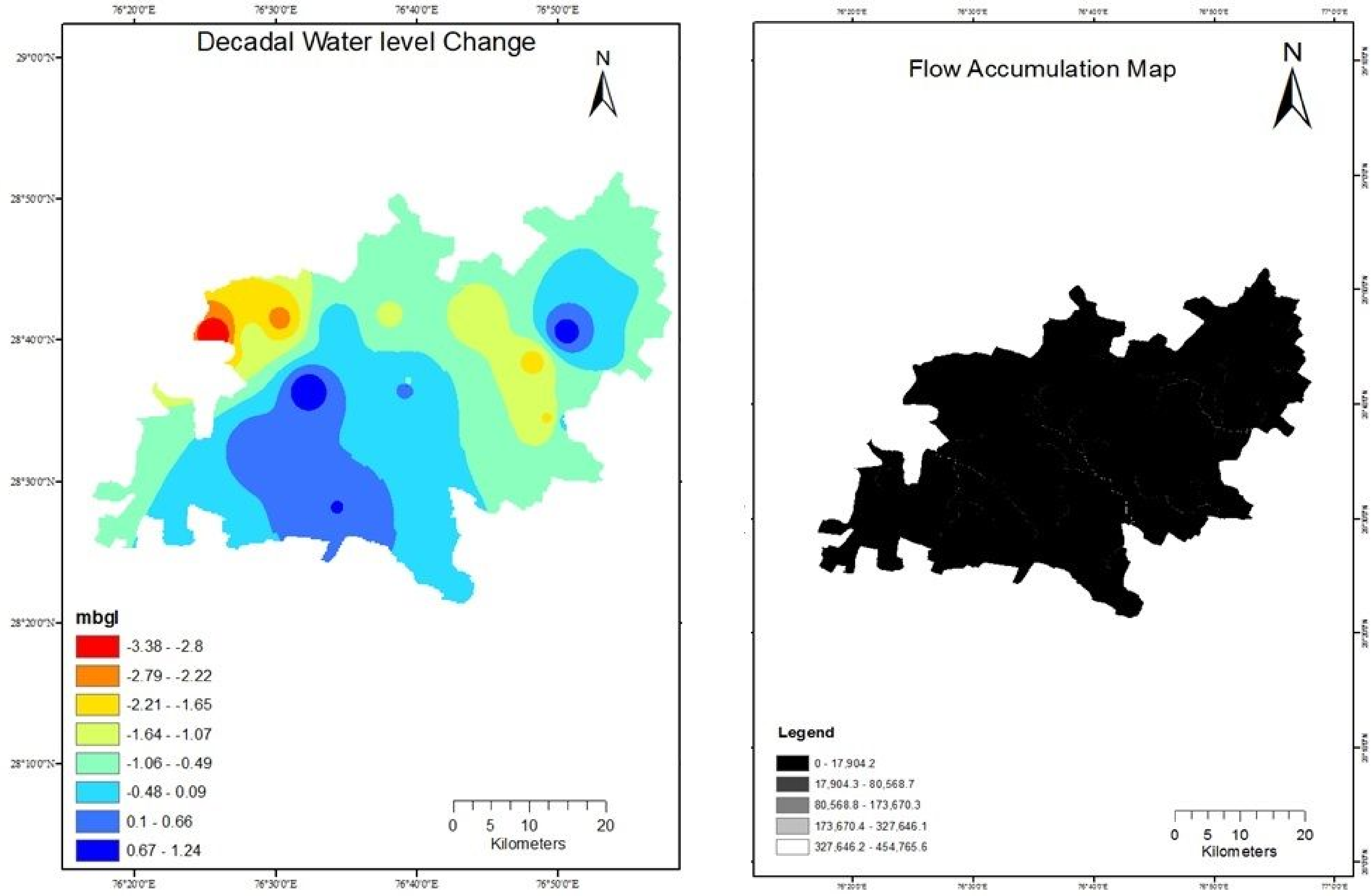

Figure 9

Map showing (a) Decadal water level Change (b) Flow Accumulation

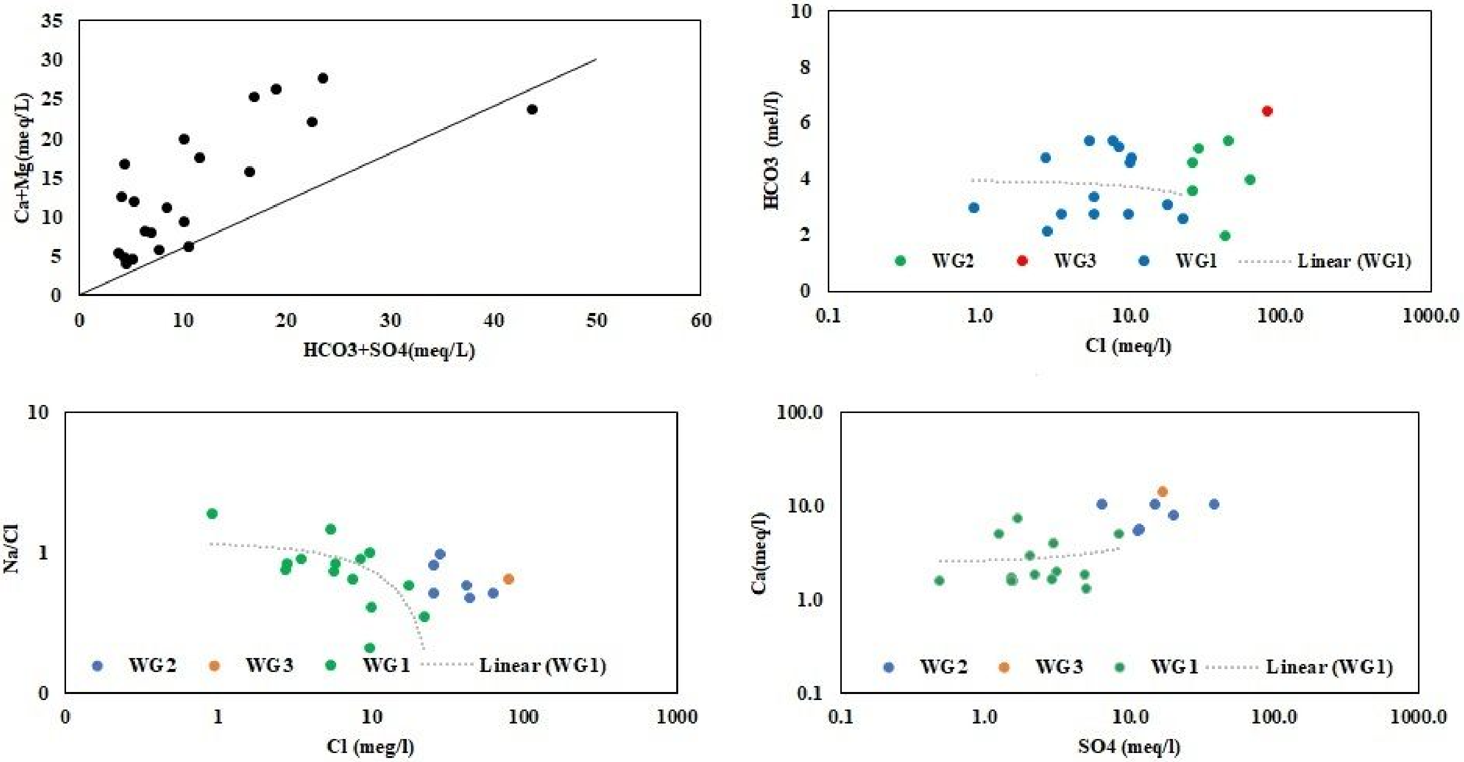

Figure 10

Hydrochemical relationships of (a) Ca2++Mg2+ vs HCO3 -+SO4 2- (b) HCO3 vs Cl (C) Na/Cl vs Cl and (d) Ca vs SO4