Research Article

Seasonal, Spatial and Vertical Variations in Groundwater Chemistry of Karimnagar District, Telangana State, India

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Abstract

Hydrodynamics play crucial role in controlling the water chemistry and by virtue of its dipolar and amphoteric character the oxidane consistently undergoes physico-chemical modifications. It becomes imperative to study and chronicle these changes holistically which could aid in initiating corrective measures and optimizing the utilization this dwindling resource. Three-dimensional approach is adopted to record the variations in water chemistry in multiple aquifer system of Karimnagar District. The major ion chemistry of groundwater obtained from about 64 monitoring wells in pre and post-monsoon seasons of the year 2014 indicate distinct raise in ion concentration in post-monsoon. Na^+, K^+ and Cl^- have increased up to +58% and Ca^{2+}, Mg^{2+} from +19 and +26 respectively in post-monsoon than pre-monsoon samples. Low rainfall (-23%) together with enhanced groundwater extraction might have aggravated the ionization of formation waters. Incongruent spatial distribution of chemical constituents is noticed in groundwater; it could be due to dissimilarity in aquifer mineralogy but it is evident that other hydro geochemical factors were also controlling the water chemistry. K^+ content has increased by about 15% whereas Cl^-, NO_3^- and F^- are distinctly reduced by about 35 to 45% in samples of sedimentary rocks than those of granite aquifers.

Vertical variation in water chemistry is in concurrence with for depth of well-penetration. Na^+, Cl^- and Mg^{2+} have decreased while CO_3^{2-}, SO_4^{2-} and NO_3^- have increased in wells developed down to 60m than those of 50m. Na^+ has marginally increased (6.3%); K^+ (-65%) and NO_3^- (-42%) have drastically decreased in wells of 90m deep than those of 60m. Aquifer mineralogy and hydraulics might be governing the groundwater quality at different depths. Water facies study show that $Na-HCO_3$ type of water is predominant in both seasons followed by $Mg-HCO_3$ with Cl type, and $Ca-Cl/HCO_3$ type. The CAI-1 and CAI-2 are negative in about 80% of the samples indicating the ion exchange between Na^+-K^+ in water and Ca^{2+}-Mg^{2+} in rocks had resulted in enrichment of alkali earths in groundwater. Correlation matrix and Gibbs plot support that ion enrichment of groundwater by water-rock interaction of aquifer matrix apart from addition of solute loaded recharge water.

Introduction

Water being a dynamic resource under goes rapid changes in its physical as well as chemical form owing to is disposition. Hydrological cycle is true and visible example of its physical changes. Chemical changes in aqueous system can be demonstrated by multipronged approach to study its chemical makeup. Many factors control the ionic composition of the water more particularly the groundwater which is highly mineralized. Broadly the host rock environment, aquifer hydraulics and change in storage as a result of seasonal changes govern the groundwater chemistry. Water chemistry variations within an insitu formation even in close proximity, similarly in an aquifer confined to different fracture system are evident [1-2]. Flow dynamics and surface drainage network apart from lithological heterogeneities determine the spatial variations in water chemistry.

Favorable recharge conduits and supply source from precipitation, irrigation return flow could alter the aquatic chemistry in the sub-surface domain which can add or deplete some chemical

constituents. Massive or impervious formations, aquifuge layers hinder the vertical percolation of recharge water leading to development of lateral flow path. Wells in such formations do not exhibit distinct chemical variability. Often the groundwater in bore wells represents the mixed waters encountered at different features /zones. Study of the vertical variability in water chemistry is a challenge always unless depth-specific sampling is possible. Owning to these shortcomings such studies are rarely attempted [3-6].

The studies related to variations in water chemistry are very popular among hydrogeochemists. Apart from them, wide spectrum of scientists belonging different disciplines are engaged in in-depth research on this topic. Contribution to science on this domain covering different hydrogeological environments is not only abundant but also continuous particularly in the last few decades [3,7,8-22].

Though variations in water chemistry is one of the widely studied world over, the hinterlands of Karimnagar district are left unexplored in this aspect. To bridge the knowledge, gap an attempt is made through this paper to evaluate the multi-directional (spatial-temporal-vertical) changes in the hydrogeochemistry of the district. The selected area is opt for such study as it is endowed with varied geological formations, multi-layer aquifer system and has many mines, industries apart from large extent of agriculture land.

The objective of the Paper is to chronicle the variations in species abundance of groundwater between pre-and post-monsoon seasons, different geological formation and among the multiple aquifers pertaining to Karimnagar District. It is also aimed at stoichiometric assessment of the mechanisms governing the ionization of groundwater. Enormous data on water chemistry is generated over the years by different agencies but rarely any attempt is made to keenly evaluate the results to chronical the changes, if any, in ion concertation of groundwater confined to different aquifers or within the same aquifer. Development of data base related to water chemistry variations would benefit the stake holders in effective utilization of the water resource.

It will also spotlight on the deterioration in water quality apart from indicating the source and causes of contamination. The proposed ensemble models successfully delineated the influences of seasonal variations and anthropogenic activities on groundwater hydrochemistry and can be used as effective tools for forecasting the chemical composition of groundwater for its management [16]. Usually the water quality monitoring is carried on wide spectrum of wells representing different hydrogeological environments for different seasons. Unless these results are analyzed and interpreted for the benefit of the common man the very purpose of monitoring is lost. Data output and storing without its in-depth analysis and sprouting of viable solutions shall be a futile exercise, hence in this paper efforts were made to promote the fruitful utilization of the water chemistry data.

The different methods of identification of the changes in chemical composition of the groundwater along with reasons and causes were demonstrating by utilizing the pre and post-monsoon data of multiple aquifers. The major ion chemistry data obtained for the purpose belongs to observation wells (piezometers) which were drilled exclusively for monitoring of water levels and quality by the State Govt. under the National Hydrology Project. These wells represent the multi-layer aquifer systems of the Karimnagar district which include both phreatic and semi-confined aquifers belonging to granitic and sedimentary terrains.

Location

The study area, Karimnagar district (erstwhile) belongs to Telangana State of India. The district lies approximately between the latitudes 17° 50' and 19° 05'N and longitudes 78° 29' and 80° 22'E. Karimnagar district is bounded by Madhya Pradesh State in the east, Nizamabad district in the West, Warangal and Medak districts in the South and Adilabad district in the North (Figure 1). The general elevation is 280 m amsl. The district forms part of the Godavari river basin. The river enters the district at Kandukurthi village runs for a distance of 283 km forming the northern and eastern boundary of and leaves the district at Muknur village. The entire district is mainly drained by Manair River, a tributary of river Godavari. The area under forest cover constitutes 21.50% of total geographical area of the district. Out of 5.31 lakh ha of net area sown in the year 2012, only 45% is under irrigation by different sources. 25% of the irrigated area is covered by surface water sources, 65% of the area is irrigated through groundwater sources and the remaining by other sources. The main crops cultivated are rice, maize, green gram, chilies, turmeric, and cotton and ground nut [23].

Telangana State in India

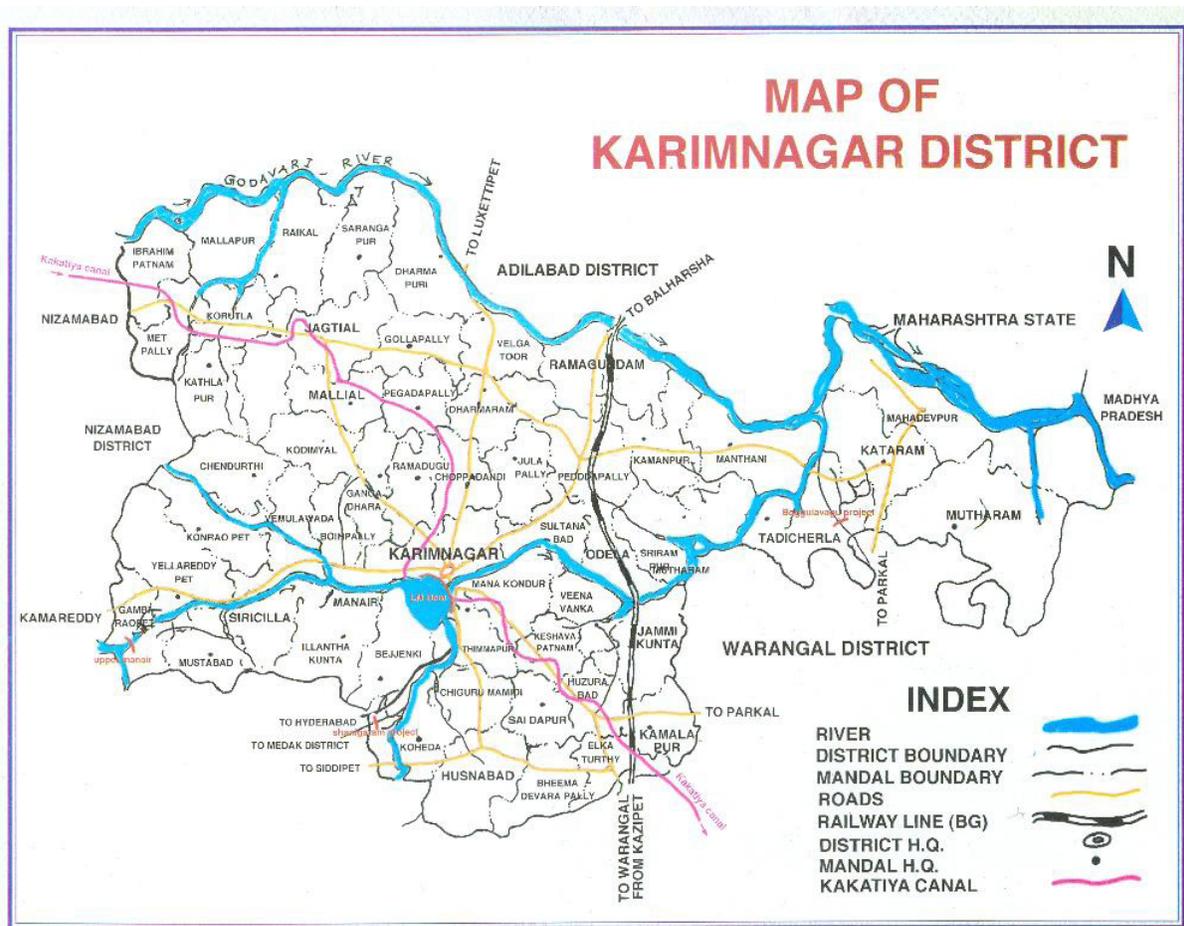Districts in Telangana State

Karimnagar Distrcit with majour towns

Figure 1: Key Map with physical features of Karimnagar District.

Rainfall

The average annual rainfall of the district is 950 mm, which ranges from nil rainfall in December to January to 250 mm in July. July and August are the wettest months of the year. The season-wise distribution of rainfall is, 83% in southwest monsoon, 11% in northeast monsoon, 0.6% in winter and 5.4% in summer. Analysis of annual and seasonal rainfall data for the period 15 years from 1999 to 2014 indicate that the area received less than Long Period Average (LPA) rain intermittently in 10 years, the rainfall deficit was >20% in 6 years (Table 1). In the studied year (2014) the rainfall was far less than the LPA, the deviation from annual rainfall was -23%; in SW monsoon it was -28% and -83% in NE monsoon.

Year	Actual rainfall (mm)			% departure from LPA		
	Annual	SWM	NEM	Annual	SWM	NEM
1999	785	712	30	-17	-10	-70
2000	974	922	5.00	3	16	-95
2001	744	585	106	-22	-26	5
2002	662	548	45	-30	-31	-56
2003	723	591	109	-24	-25	8
2004	871	575	88	-8	-27	-13
2005	1644	1215	217	73	53	114
2006	1511	1231	109	59	55	7
2007	947	850	49	0	7	-52
2008	898	769	15	-5	-3	-85
2009	643	486	123	-32	-39	21
2010	1454	1223	196	53	54	94
2011	747	674	6.90	-21	-15	-93
2012	1047	919	108	10	16	6
2013	1428	1073	270	50	36	166
2014	733	572	17	-23	-28	-83
LPA	950	792	101			

SWM: Southwest monsoon;   NEM: Northeast monsoon;   LPA: Long period average (Normal rainfall)

Table 1: Analysis of annual and seasonal rainfall data.

Hydrogeology

The major rock types occurring in the district are granite gneisses which occupy about two thirds area of the district. Rest of the district, especially the northern corner, is covered by sandstone, limestone, shale, quartzite rocks. Alluvium comprising sand, silt and clay occurs along the banks of the river Godavari down to a maximum depth of 20 m, bgl near Mahadevpur (Figure 2). The shallow aquifers confined to the weathered zone have very limited yields and are exploited through open wells. The deep fractured aquifer was developed through bore wells. The fractured aquifers are potential down to 100 m depth in general, and are encountered only along the lineaments. The discharge of the successful bore wells ranges from 0.5 lps to 3 lps [24].
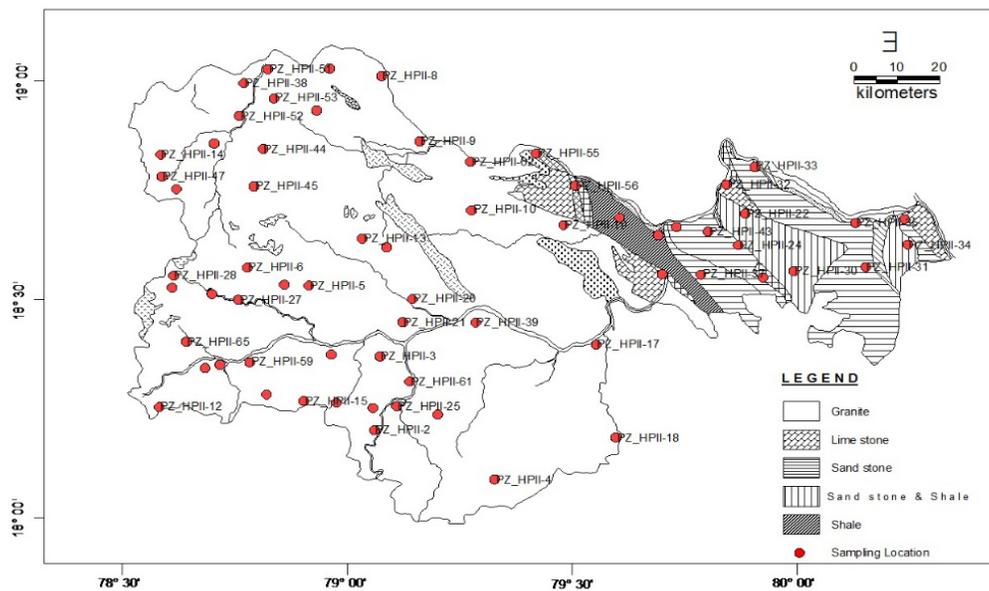

Figure 2: Locations of sample sources.

[HPII-Open wells monitoring initiated in Hydrology Project II; PZ_HPII- Piezometers (Bore wells) developed in Hydrology Project Phase II]

Martial and Methods

The groundwater sampling and analysis was done by Telangana State Ground Water Dept. (TSGWD). The water samples were collected from 65 piezometers of TSGWD after thorough purging of the wells in 1-liter capacity PVC bottles in early June 2014 for pre-monsoon and in October for post-monsoon season (Figure 2).

The water analysis for determination of major chemical ions (Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, HCO_3^-, NO_3^-, SO_4^{2-}, F^-), apart from pH, electrical conductivity and total hardness was carried out in chemical laboratory of TSGWD following APHA procedures [25]. Classical method of analysis was adopted for the analysis of select ions and instruments were used for determination of certain parameters. For the present work water chemistry results for 64 wells pertaining two seasons of 2014 were obtained from TSGWD. The data was organized, analysed and interpreted by prepared tables, graphs, and plots using MS Excel to delineate the water chemistry variations and infer the hydrogeochemical processed involved.

Results and Discussions

In the pre-monsoon pH vary from 7.08 to 8.81 showing slightly alkaline nature, with a mean value of 8.05, having a Standard Deviation (SD) of 0.31. Electrical conductivity value has a drastic variation ranging between 202 and 2711 µS/cm with a mean value of 840 µS/cm and the SD is 414. The total hardness ranges from 100 to 640 mg/l having a mean of 537 mg/l with SD of 101. In the post monsoon season the pH value varies from 7.30 to 8.85 with a mean of 8.23 having a 0.32 SD. The EC values range between 311 and 6190 µS/cm, with a mean of 1215 µS/cm and having high SD of 955. High (>3000 µS/cm) EC at few locations (Vavilala, Dacharam and Guggilla) indicate the influence of local contamination of groundwater. The TH values ranges from 120 to 1240 mg/l with a mean of 315 mg/l having SD of 192. The analyzed cations and anions vary widely, among them Mg^{2+}, Na^+, K^+, Cl^- and SO_4^{2-} are abnormally high at few locations. Among anions, NO_3^- concentration range from 0.32 to 69.27 mg/l in pre-monsoon and 0.2 to 109 mg/l in post-monsoon. The fluoride content varies from 0.05 to 3.55 mg/l in the post monsoon, about 11 samples have F^- in high (>1.5mg/l) concentration. The mean values and varaitions in the pre and post-monsoon of the analyzed parameters are given in the (Table 2 and Figure 3a).

Parameter	Units	Pre-Monsoon (N=63)	Post-Monsoon (N=63)	SD	Variation in Concentration From Pre to Post-Monsoon
pH		8.05	8.23	0.12	2%
EC	µS/cm	840	1215	265	45%
TDS	mg/l	537	778	170	45%
TH		255	315	42	23%
Ca		44	53	6	19%
Mg		35	45	7	26%
Na		87	134	33	54%
K		16	26	7	58%
CO_3		6	23	12	271%
HCO_3		188	203	10	8%
Cl		101	155	38	53%
SO_4		52	110	41	110%
NO_3		10	14	3	45%
F		NA	0.90		
NA: Not analysed					

Table 2: Mean and seasonal (pre and post monsoon 2014) variation of analysed parameters (mean).
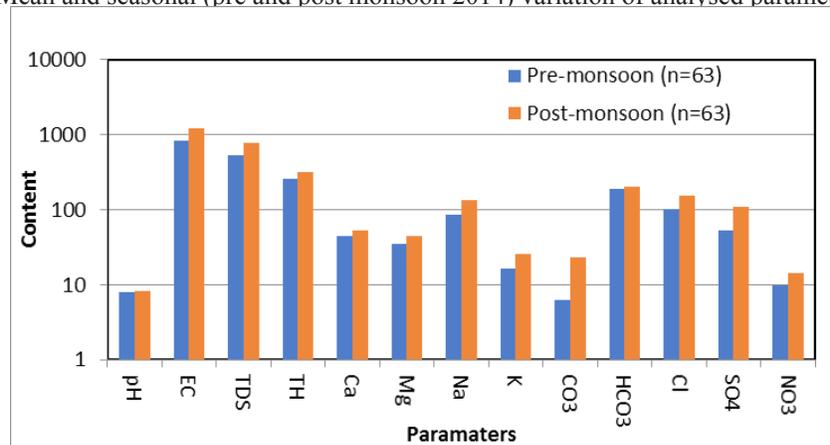

Figure 3a: Seasonal Variation in water chemistry.

Classification of Groundwater

The groundwater can be classified based on EC as type I, if the enrichments of salts are low (EC 1,500 µS/cm); type II, if the enrichment of salts are medium (EC 1,500 and 3,000 µS/cm); and type III, if the enrichments of salts are high (EC 3000 µS/cm [26]. In pre-monsoon 95% of samples belong to types I and rest to type II, in post-monsoon too EC did not exhibit significant variation, 92% samples have <1500 µS/cm falling in type I category and rest in type II. A more detail classification of water based on EC is proposed for better comprehension of mineralization of groundwater (Table 3). According to the proposed classification majority of the samples fall in Type 2 category, which have EC ranging between 500 and 1000 µS/cm.

Type	EC (µS/cm)	% of samples	
		Pre-monsoon	Post-monsoon
1	<500	17	36
2	501-1000	51	45
3	1001-1500	27	11
4	1500-3000	5	8
5	>3000	0	0

Table 3: Classification groundwater based on EC.

The groundwater is categorized based on TDS content, applying Davis and De Wiest [27] and Freeze and Cherry [28] methods. Majority of the samples in both the seasons fall within desirable and permissible limit for drinking water as the TDS is <1000 mg/l (Table 4a and 4b). Samples having TDS above 1000mg/l are more in post-monsoon than pre-monsoon exhibiting impact of evapotranspiration on ionization of groundwater. Based on the total hardness (TH as $COCO_3$) the groundwater samples of the both the seasons are classified applying the methods proposed by Durfor and Becker [29]; Sawyer and McCarty [30].

TDS (mg/l)	Water type	% of samples	
		Pre-monsoon	Post-monsoon
<500	Desirable for drinking	59	36
500-1000	Permissible for drinking	36	45
<3000	Useful for irrigation	5	17
>3000	Unfit for drinking and irrigation	0	2

Table 4a: Classification of groundwater based on TDS (Davis and De Wiest method).

TDS (mg/l)	Water type	% of samples	
		Pre-monsoon	Post-monsoon
<1000	Fresh	95	81

1000–10,000	Brackish	5	19
10,000-100,000	Saline	0	0
>100,000	Brine	0	0

Table 4b: Classification of groundwater based on TDS (Freeze and Cherry method).

Majority of the water fall in hard (63% in pre-monsoon and 55% in post-monsoon - Sawyer and McCarty method) to very hard (78% in pre-monsoon and 83% in post-monsoon - Durfor and Becker method) category as TH is >200 mg/l in many samples (Table 5a and 5b). Ca and Mg based minerals of granitic aquifer material might be responsible for higher TH in groundwater. The groundwater has gained marginally more hardness in post-monsoon which could be the resultant of recharge waters getting enriched in alkali earths in initial stages of infiltration processes.

Total Hardness ($CaCO_3$) mg/l	Water type	% of samples	
		Pre-monsoon	Post-monsoon
0 - 60	Soft water	0	0
60 - 120	Moderately hard water	3	6
120 -180	Hard water	19	11
> 180	Very hard water	78	83

Table 5a: Classification of groundwater based on TH (Durfor and Becker method).

Total Hardness ($CaCO_3$) mg/l	Water type	% of samples	
		Pre-monsoon	Post-monsoon
<75	Soft	0	0
75–150	Moderately high	10	8
150-300	Hard	63	55
>300	Very Hard	27	37

Table 5b: Classification of groundwater based on TH (Sawyer and McCarty method).

Soltan [31] has proposed categorization of groundwater based on the meq/l content of Cl^-, SO_4^{2-}, and HCO_3^-. The water is Normal Chloride type if Cl^- is <15 meq/l, Normal Sulfate type if SO_4^{2-} is <6 meq/l, and Normal Bicarbonate type if HCO_3^- varies between 2 and 7 meq/l. Distribution of groundwater samples based on the Soltan's classification has indicated that all the samples in pre-monsoon and majority in post-monsoon are of Normal Sulfate type (94% in post-monsoon), followed by Normal Chlorite type (96% in post-monsoon), whereas 76% in pre-monsoon and 70% in

post-monsoon are of Normal Bicarbonate type.

The Base Exchange indices [32] determined by using the r1=Na$^+$- Cl$^-$/SO$_4^{2-}$ could be applied for the further classification of groundwater. The water can be grouped as Na$^+$-HCO$_3^-$ type if r1 > 1 and Na$^+$- SO$_4^{2-}$ type with r1 < 1. 59% samples in pre-monsoon and 23% in post-monsoon are of Na$^+$- SO$_4^{2-}$ type as r1 < 1 and rest are of Na$^+$–HCO$_3^-$ type. High percentage (77%) of bicarbonate sulphate water in post-monsoon substantiate that rainfall of monsoon constitute bulk of recharge water. Variations in water chemistry in post-monsoon are of the effect of different water inputs (monsoon rain, irrigation and downward percolation from surface water impounds) to the groundwater system [22]. It also establishes that the regular replenishment of aquifer is occurring through prevailing conductive recharge and discharge conditions of the area.

Water Chemistry Variations

There are many variables that influence groundwater chemistry. Aquifer rock type, dissolvable minerals present and their concentration, groundwater flow paths through the aquifer, contact or residence time, and recharge rates are examples of variables that influence groundwater quality. Other factors such as well depth, use, and well construction can also control water quality in a well. Apart from these geogenic factors, the external addition of chemical constituents due to anthropogenic activity unduly influences the aquifer chemistry.

Factors Affecting Groundwater Chemistry Variations

Understanding of the factors that influence the groundwater chemistry can help to make decisions on well depth and the best utilization of groundwater for a particular use. There are few important aspects that affect ground water chemistry:

- Temporal (Time or sequential variations).

- Geological formations (Aquifer mineralogy).

- Aquifer Disposition-Depth from ground surface (Aquifer hydraulics).

In concurrence with the factors affecting the water chemistry a three-dimension approach is adopted to evaluate the water chemistry variations, they include the seasonal, spatial and vertical (depth-wise) changes. This approach will convey the water chemistry modification in an aquifer holistically.

Seasonal Variation (Temporal)

The seasonal change is studied by comparing the major ion chemistry results of pre-monsoon and post-monsoon 2014 since the water samples were collected from the same wells in both the seasons. All tested parameters significantly raised in post-monsoon which is uncommon and incongruent. The percentage changes between pre and post-monsoon displays that CO$_3^{2-}$ and SO$_4^{2-}$ have distinctly increased, whereas the HCO$_3^-$, alkali earths and TH show moderate raise. The pH has increased from 8.05 to 8.23 between two studied seasons (Table 2). Na$^+$, K$^+$ and Cl$^-$ have varied over time by up to +58% and Ca^{2+}, Mg^{2+} from +19 and +26 respectively. Low rainfall (-23%) together with enhanced groundwater extraction might have aggravated the ionization of formation waters. Descending dispersion of accumulated soil salts through percolating pore water and irrigation return flow could have also contributed ion enrichment of groundwater in post-monsoon season [22].

Climatic variations such as annual rainfall and evaporation rates also play an important role in groundwater chemistry. In semi-arid regions discharging groundwater often evaporates as it approaches the surface. The minerals from the water are deposited in the soil, creating a salt buildup. Precipitation infiltrating through the soil can redispose the salts, carrying them back into the groundwater. For example, in east central and southern Alberta where annual precipitation is from 25-40 cm (10-16 in.) and the evaporation rate is high, TDS are about 2500 parts per million (ppm). In areas with higher precipitation and lower evaporation rates, precipitation that reaches groundwater is less mineralized. For example, in western Alberta where annual precipitation is more than 45 cm (18 inch.) groundwater in surficial deposits contains less than 800 ppm of TDS [33].

Spatial Variations (Geological)

The chemical composition of groundwater varies depending on the geological location of the sampled wells. The Archaean Dharwar group of rock types occupy about two thirds area of the district. The groundwater occurs under unconfined conditions in weathered zone and under semi confined conditions in the fractures and fissures. The district is endowed with complex rock types in about 20% area in north and is underlain by the semi-consolidated rocks comprising quartzites, sandstones and lime stones, shales belong to Purana to Kota formations. Spatial heterogeneity in water chemistry can be best studied by segregating the samples into two broad geological formations viz. granite and sedimentary aquifers and comparing the variation in the concertation of the analyzed

parameters. About 46 samples were collected from granitic aquifer and 17 from sedimentary. Significant differences in concentration in samples collected from the two aquifer types were identified in many of the tested parameters (Table 6).

Parameter	Units	Pre-monsoon			Post-monsoon		
		Granite aquifers (n=46)	Sedimentary aquifers (n=17)	Difference in concentration between Granite and Sedimentary aquifers	Granite aquifers (n=46)	Sedimentary aquifers (n=18)	Difference in concentration between Granite and Sedimentary aquifers
pH		8.04	8.09	1%	8.24	8.18	-1%
EC	µS/cm	902	671	-26%	1303	976	-25%
TDS	mg/l	577	430	-26%	834	625	-25%
TH		267	222	-17%	345	231	-33%
Ca^{2+}		45	41	-8%	53	52	-1%
Mg^{2+}		38	29	-23%	52	25	-53%
Na^+		95	63	-34%	144	107	-25%
K^+		18	11	-36%	25	28	14%
CO_3^{2-}		6	6	-7%	23	22	-6%
HCO_3^-		196	166	-15%	206	197	-4%
Cl^-		112	73	-35%	172	109	-36%
SO_4^{2-}		55	46	-17%	117	91	-22%
NO_3^-		11	6.14	-45%	17	8	-54%
F^-		NA	NA		1.03	0.58	-43%
NA: Not analysed							

Table 6: Seasonal (pre and post-monsoon 2014) variation of analysed paramaters in different aquifers.

The pH has raised marginally in samples of sedimentary rocks belonging to pre-monsoon seasons whereas the same has reduced in post-monsoon. Concentrations of all other examined ions are higher in granite aquifers than those of sedimentary. Apart from geological considerations large difference in the sample population could also one of the reasons for the incoherent distribution of chemical constituents. K^+ content has increased by about 15% in samples of sedimentary rocks than those of granite terrain during post-monsoon. Anthropogenic causes could be responsible for this unusually high K^+ in sedimentary aquifers as K-rich minerals will be very low in these bedded rocks. Large difference can be noticed in case of NO_3^- (11.20 mg/l in samples of granites and 6.14 mg/l in sedimentary aquifers in pre-monsoon) and F^- (1.03 mg/l in granite aquifers and 0.58 mg/l in those of sedimentary rocks) among samples of granite and sedimentary terrain in two seasons. Concentration of Cl^- is distinctly low (-35%) in both the seasons in samples from sedimentary rocks than those of granite. Cl^- concentrations tend to change in accord with sedimentary layer structures [21]. Apart from mineralogical variations the lithologic structure with sand-clay alternation, relatively thick clay layer might be responsible for distinct ion content in sedimentary rock aquifers [19]. High ion strength in

granite aquifers can be accounted both for favorable hydrological and geological conditions. Water composition in granites was affected by inter-connected network of fractures which form good conduits for transmission of percolating pore water facilitating significant lateral flow [34]. Recharge water with ion load apart from aquifer matrix mineralogy might be responsible for higher accumulation of chemicals in wells of granite terrain. Low fluoride in water samples belonging to sedimentary rocks is in concurrence with their minerology. Wide variation in water chemistry of the groundwater occurring granites as well as sedimentary aquifers infers the influence of aquifer stratigraphy on groundwater flow paths and low-permeability layers of sediments followed by absence of gradient flow.

In addition to the aquifer hydraulics, watershed parameters have played decisive role in groundwater mineralization. Groundwater inflow is largely governed by regional groundwater flow paths [35]. The quality of groundwater is altered by the land use activities that take place in study area apart from the hydrological components like drainage pattern, recharge-discharge zones etc. Since the sampled wells are spread over entire district and are identified based on the political boundaries rather than

hydrogeological considerations the impact of hydrological features and land-use on water chemistry is not explored.

Vertical Variation (Depth-Wise)

Well depth can affect both the quality and quantity of water pumped from a well. The quality of water in a well is influenced by the depth of well penetration and aquifers encountered. The longer the groundwater takes to move through the sediments, the more mineralized it becomes. Thus, shallow groundwater aquifers have a lower level of mineralization, or Total Dissolved Solids (TDS), than deeper aquifers. Water from deeper groundwater aquifers typically has a much longer sub-surface movement and residency time and thus it is usually more mineralized. While shallow wells have lower levels of TDS, they do have higher levels of calcium, magnesium and iron than deeper wells. High levels of these minerals make the water "hard." Deeper wells have higher levels of sodium and lower levels of hardness, making the water "soft." The reason is that deeper sediments and rock formations contain higher levels of sodium and as water moves downward through the sediment and rock formations, a natural ion exchange process occurs.

Depth-wise categorization of water chemistry data for both pre and post-monsoon was carried out. The samples are grouped into three configurations based on the total depth of the monitored wells viz. ground level or 0 to 50m; 0 to 60m and 0 to 90m. The physico-chemical characters of groundwater pertaining to each group in two different seasons are presented in (Table 7). In pre-monsoon no marked change in water chemistry is noticed among wells penetrating down to 50m and 60m. Na^+, Cl^- and Mg^{2+} have decreased whereas CO_3^{2-}, SO_4^{2-} and NO_3^- have increased in wells developed down to 60m than those of 50m. K^+ concentration has risen from 8.2 to 31mg/l and SO_4^{2-} by 8mg/l emphasizing that the aquifer material and water-rock interaction played significant role in ionization of formation water. Depth-wise change in concentration of redox-sensitive elements is significant [3]. Na^+ has marginally increased (6.3%) and all other ions concertation has reduced in wells of 90m deep than those of 60m. K^+ (-65%) and NO_3^- (-42%) have drastically decreased in deeper (90m) wells than wells tapping zones down to 60m.

Para meter	Units	Pre-monsoon			Post-monsoon			Pre-monsoon		Post-monsoon	
		Depth < 50m (n=23)	Depth < 60m (n=21)	Depth < 90m (n=13)	Depth < 50m (n=23)	Depth < 60m (n=21)	Depth < 90m (n=13)	% difference in concentration between 50 and 60m depth	% difference in concentration between 60 and 90m depth	% difference in concentration between 50 and 60m depth	% difference in concentration between 60 and 90m depth
pH		8.00	8.10	8.02	8.20	8.30	8.00	1%	-1%	1%	-4%
EC	µS/cm	887	889	765	1406	967	1284	0%	-14%	-31%	33%
TDS		568	569	489	900	619	822	0%	-14%	-31%	33%
TH		277	265	227	345	286	317	-4%	-14%	-17%	11%
Ca^{2+}		47	46	39	54	50	56	-1%	-15%	-7%	12%
Mg^{2+}		39	36	31	51	39	43	-8%	-14%	-24%	10%
Na^+		101	79	84	162	91	150	-22%	6%	-44%	65%
K^+	mg/l	8.20	31	11	25	29	28	278%	-65%	16%	-3%
CO_3^{2-}		4.60	7.00	6.00	18	28	15	52%	-14%	56%	-46%
HCO_3^-		189	193	189	216	176	217	2%	-2%	-19%	23%
Cl^-		121	100	86	204	92	175	-17%	-14%	-55%	90%
SO_4^{2-}		51	59	53	125	86	116	16%	-10%	-31%	35%
NO_3^-		11.00	12.00	7.00	18.00	12.00	14.20	9%	-42%	-33%	18%
F^-		NA	NA	NA	1.00	1.00	0.80			0%	-20%
NA: Not analysed											

Table 7: Depth-wise variations of analysed paramaters.

Lack K-minerals in aquifer material in deeper zones and massive impermeable layers can be reasoned for decrease in K^+ and NO_3^- in descending transition zones. Moderate NO_3^- concentrations suggest that significant lateral flow prevented NO_3^- enrichment [36]. Uneven distribution of NO_3^- in different depth zones could be due to combined effects of the historical NO_3 leaching and denitrification, with dispersive mixing into the pristine groundwater residing deeper in the aquifer [23]. The concentrations of major cations also varied by > 14% in these deep (90m) aquifers.

Dilution effect due to the influx of groundwater from potential zones between 60 and 90m could the possible reason for reduction in concertation of many analyzed ions in deep wells. In post-monsoon season too similar vertical variations in water chemistry can be noticed. Significant reduction in most of the analyzed parameters can be attributed to the effect of different water inputs (monsoon rain, irrigation and downward percolation from surface water impoundments) to the groundwater system [22]. The well-interconnected fracture system, continuous addition from tope zones could be replenishing aquifers as apparent by increase in CO_3^{2-} in 0-60m zones than 0-50 zones. The Variations in ion content between wells of 0-60 and 0-90 depth are very high, except CO_3^{2-} (-46%) and K (-3%) all other tested parameters have risen expressively.

Abnormal increase of Na^+ and Cl^- by 65% and 90% respectively more specifically in post-monsoon season indicate leakage from tope zones and mixing of contaminants with recharge water and its penetration down to deeper aquifers. Deeper groundwater inputs increased nonlinearly with drainage area [18]. Leaching of salts from the unsaturated zone also has a major impact on groundwater quality during the rainy season [37]. It indicates the importance of mixing under natural and/or anthropogenic influences [38]. The study confirms the inter-connectivity among different zones of the aquifers and lack of distinct, separate, layered aquifers within granite and sedimentary formations [39].

Hydrogeochemistry

Analyzing samples of well water for its chemical composition not only determines its suitability for various uses, but also provides an insight into processes which are responsible for mineralization of groundwater by the hydrogeochemistry study [40-45]. It uses the waters chemistry as a tool to decipher thermodynamic processes the groundwater underwent along its flow path. The chemical composition of groundwater is determined by a number of factors. These include the mineralogy of the rock types in catchments and aquifers media, overlying land uses, proximity to the coast, source of recharge water, soil type, aquifer hydraulics and the residency time etc. The quantity and type of minerals dissolved depend on the chemical composition and physical structure of the rocks as well as the hydrogen-ion concentration (pH) and the redox potential (Eh) of the water. Carbon dioxide in solution, derived from the atmosphere and from the organic processes in the soil, assists the solvent action of water as it moves underground. The major ion results of the district are used to evaluate the processes controlling water chemistry.

Ionic Dominance Pattern

The ionic dominance pattern for pre and post-monsoon seasons determined using mean concentration (meq/l) of the tested ions is presented in (Table 8). In both seasons Na^+ is the most dominating ion followed by HCO_3^- in pre-monsoon and Cl^- in post-monsoon. Among the cationic concentrations sodium is the dominating ion in pre and post-monsoon seasons with mean of 3.65 and 5.73 meq/L, respectively, followed by calcium (means: 2.13 and 2.58 meq/L), magnesium (means: 2.82 and 3.62 meq/L), and potassium (means: 0.40 and .64 meq/L). The hydrochemistry of cationic dominance pattern points out that the dissolution and base-exchange processes control the levels of cationic concentrations in groundwater.

Ion dominance	Ionic dominance (meq/l)									
Pre- monsoon	Na^+	HCO_3^-	Mg^{2+}	Cl^-	Ca^{2+}	SO_4^{2-}	K^+	CO_3^{2-}	NO_3^-	F^-
	3.65	2.99	2.82	2.77	2.13	1.06	0.40	0.20	0.15	NA
Post-monsoon	Na^+	Cl^-	Mg^{2+}	HCO_3^-	Ca^{2+}	SO_4^{2-}	CO_3^{2-}	K^+	NO_3^-	F^-
	5.73	4.30	3.62	3.28	2.58	2.26	0.75	0.64	0.23	0.05
% ion content (meq/l)										
% ion content	Ca^{2+}	Mg^{2+}	Na^+	K^+	CO_3^{2-}	HCO_3^-	Cl^-	SO_4^{2-}	NO_3^-	F^-
Pre- monsoon	13.16	17.42	22.6	2.48	1.24	18.48	17.1	6.54	0.95	NA
Post-monsoon	11.03	15.45	24.4	2.75	3.22	13.98	18.3	9.64	0.96	0.20
Seasonal variation	-2.13	-1.98	1.85	0.28	1.98	-4.50	1.20	3.09	0.01	

Table 8: Ionic dominance pattern and % content for Pre and Post-monsoon seasons.

Among the anionic concentrations bicarbonate is the dominating ion in pre and post-monsoon seasons, having a mean of 2.99 and 3.28 meq/l, respectively followed by chloride 2.77 meq/l and 4.30 meq/l, sulphate, 1.06 meq/l and 2.26 meq/l.0 meq/l. Percent ion content of Na^+ (-1.85%), CO_3^{2-} (-1.98%), Cl^- (-1.20%) SO_4^{2-} (-3.09%) has decreased in post-monsoon whereas Ca^{2+}, Mg^{2+} and HCO_3^- has increased. The seasonal variation is distinct in SO_4^{2-} and HCO_3^- (Figure 3b). The ion content and its dominance pattern in both seasons emphasize that the aquifer material due to water-rock interaction has contributed to chemical composition of the pore water.
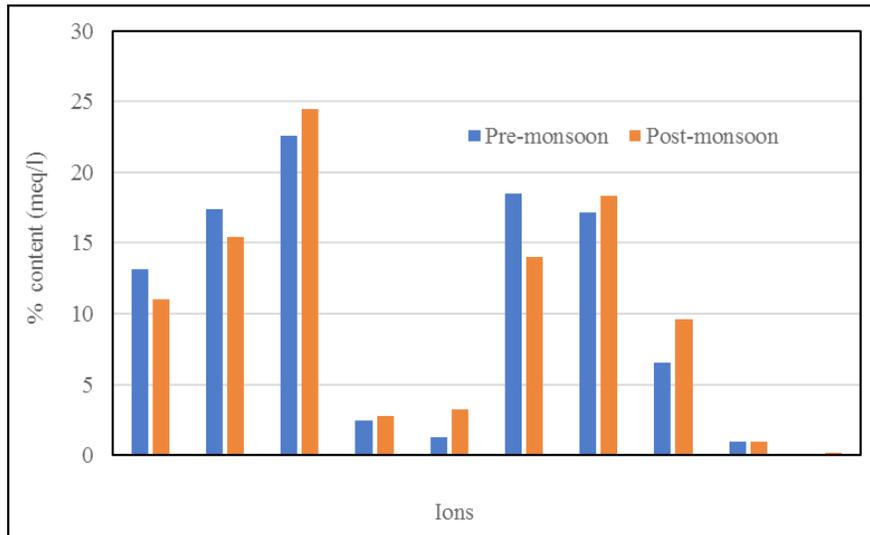

Figure 3b: Seasonal variation in % ion content.

Water Facies

The groundwater samples were plotted on the Piper [46] trilinear diagram which facilitates the cations and anions compositions of the samples to be represented on a single graph in which major groupings or trends in the data can be discerned visually. Hydrochemical zonation of water types are often used in the characterization of waters as a diagnostic tool. Piper trilinear diagram (Figure 4a and b) for the study area shows that groundwater is of mixed type as the samples can be grouped into 8 different types.
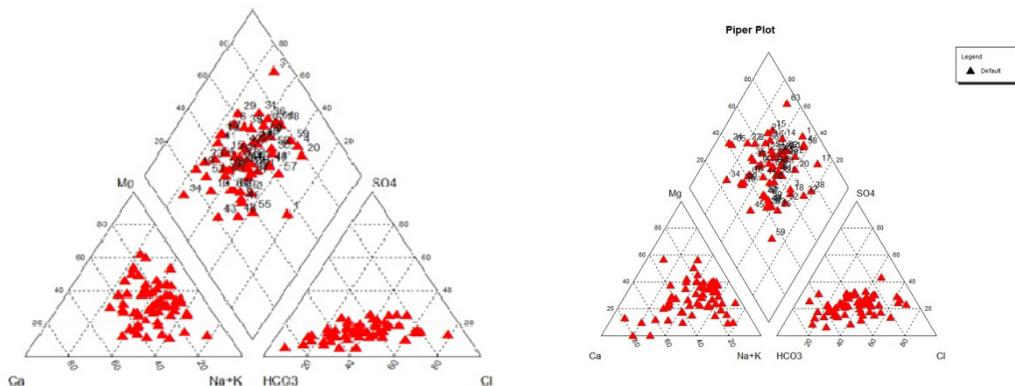
Figures 4(a-b): Piper plot for (a) Pre-monsoon (b) Post-monsoon samples.

In pre-monsoon Na-Mg-Ca/HCO$_3$ type constituting 29% of the samples, 16% are of Mg-Na-Ca type, about 13 to 6% are belong six different water types (Table 9). In post-monsoon Na-Mg-Ca/HCO$_3$ type form 30% of the samples, Ca-Na-HCO$_3$/Mg and Na-Mg-Cl type of waters are of 15% each, about 13 to 5% are belong five different water types. Basically Na-HCO$_3$ (with minor variations) type of water is predominant in both seasons.

Sl No.	Pre-monsoon		Post-monsoon	
	Water type	% of samples	Water type	% of samples
1	Na-Mg-Ca/HCO$_3$	29	Na-Mg-Ca/HCO$_3$	30
2	Mg-Na-Ca	16	Ca-Na-HCO$_3$/Mg	15
3	Mg-Na-C1	11	Na-Mg-Cl	15
4	Ca-Na-Cl/Mg	13	Mg-Ca/Na-HCO$_3$	13
5	Na-Ca-Cl/HCO$_3$	10	Na-Ca-Mg/HCO$_3$	10
6	Mg-Ca-Na/Cl	8	Na-Cl-HCO$_3$/SO4	8
7	Na-Ca-Mg	8	Ca-HCO$_3$-CO$_3$/SO4	5
8	Mg-Na-HCO$_3$	6	Ca--K/Mg-HCO$_3$	5

Table 9: Water types based on Piper plot.

Followed by Mg-HCO$_3$ with Cl type, and Ca-Cl/HCO$_3$ type. Seasonal variation in water types is only with respect to percentage of samples in different water types. The groundwater facies indicate water chemistry is controlled by ion migration followed by mixing under natural and/or anthropogenic influences (Han et. al., 2014). Multiplicity in water types reflects the prevalence of distinct hydrological processes in evolution of aqueous chemistry.

Ion Exchange

The chloroalkali index (CAI - 1 and 2) developed by Schoeller [47], relate the ion exchange process between groundwater and aquifer material. The CAI-1 and CAI-2 are negative in a majority (73%, 87% in pre-monsoon and 72%, 83% in post-monsoon respectively) of the samples indicating the ion exchange between

Na$^+$-K$^+$ in water and Ca^{2+}-Mg^{2+} in rocks had resulted in enrichment of alkali earths in groundwater [48]. Water composition was affected not only by ion exchange and dissolution equilibrium [19]. The predominant mechanism controlling groundwater chemistry proved to be the dissolution of carbonates, gypsum, and halite. Cation exchange and mixing with local recharge water are also important factors [12].

Correlation

Correlation matrix of pre and post-monsoon samples indicate that the influence of CO$_3^{2-}$ for pH. Na$^+$, Cl$^-$, SO$_4^{2-}$, NO$_3^-$ contribute more for the EC of groundwater, apart from them the effect of Ca^{2+} is significant in pre-monsoon whereas in post-monsoon Mg^{2+} influence is more than Ca^{2+} (Table 10a). Increase in major ion concentrations along the flow path, including Na$^+$, Cl$^-$, and SO$_4^{2-}$, coincide with increases in total dissolved solids [12]. Role of Na$^+$ on water chemistry is high in post-monsoon as correlation (r) for Na$^+$: Mg^{2+} is 0.82 whereas in pre-monsoon it is only 0.31. The correlation of EC-Mg^{2+} is quite lesser in pre-monsoon (0.46) than post-monsoon (0.86). Dissolution of Na$^+$-Mg^{2+} based minerals, which dominate the granite aquifers, might be contributing these cations to groundwater. High positively correlated Mg^{2+}: Cl$^-$, SO$_4^{2-}$, NO$_3^-$ in post-monsoon (>0.70) also support that recharge water is responsible for enrichment of groundwater by water-rock interaction of aquifer matrix. Good correlation (>0.6) of NO$_3^-$ with Cl$^-$, SO$_4^{2-}$ and K$^+$ substantiates that both agriculture reflow and sewerage are contributing for nitrification of groundwater (Table 10b). Contrasting r for Ca^{2+}: Cl$^-$ in pre-monsoon (0.68) and post-monsoon (0.34) is incongruent. The correlation matrix for both seasons support that groundwater is more mineralized in post-monsoon (r is >0.90 for EC: Na$^+$, Cl$^-$, SO$_4^{2-}$) which is evidently due to solute loaded recharge water.

	PH	EC	TH	Ca	Mg	Na	K	CO3	HCO3	Cl	SO4	NO3
PH	1.00											
EC	-0.18	1.00										
TH	-0.15	0.74	1.00									
Ca	-0.40	0.62	0.68	1.00								
Mg	0.15	0.46	0.76	0.04	1.00							
Na	-0.13	0.85	0.51	0.42	0.31	1.00						
K	-0.17	0.59	0.28	0.26	0.15	0.35	1.00					
CO3	0.63	-0.15	-0.11	-0.29	0.11	-0.07	-0.08	1.00				
HCO3	-0.04	0.41	0.20	0.04	0.24	0.43	0.09	-0.07	1.00			
Cl	-0.25	0.89	0.76	0.68	0.43	0.78	0.47	-0.19	0.07	1.00		
SO4	-0.15	0.88	0.63	0.59	0.33	0.70	0.66	-0.14	0.22	0.79	1.00	
NO3	-0.19	0.80	0.65	0.57	0.38	0.64	0.60	-0.10	0.17	0.67	0.76	1.00

Table 10a: Correlation matrix for pre-monsoon samples.

	PH	EC	TH	Ca	Mg	Na	K	CO3	HCO3	Cl	SO4	NO3	F
PH	1.00												
EC	-0.20	1.00											
TH	-0.23	0.87	1.00										
Ca	-0.66	0.28	0.44	1.00									
Mg	-0.01	0.86	0.94	0.11	1.00								
Na	-0.11	0.97	0.78	0.12	0.82	1.00							
K	-0.05	0.56	0.34	0.13	0.32	0.47	1.00						
CO3	0.67	0.12	0.02	-0.34	0.15	0.17	0.24	1.00					
HCO3	-0.22	0.53	0.34	-0.03	0.39	0.50	0.36	-0.04	1.00				
Cl	-0.25	0.97	0.87	0.34	0.84	0.94	0.44	0.04	0.39	1.00			
SO4	-0.13	0.94	0.77	0.26	0.76	0.93	0.57	0.15	0.37	0.92	1.00		
NO3	-0.21	0.85	0.85	0.41	0.79	0.79	0.53	0.08	0.24	0.82	0.82	1.00	
F	0.38	0.13	0.15	-0.33	0.29	0.17	-0.07	0.42	0.22	0.05	0.04	0.11	1.00

Table 10b: Correlation matrix for post-monsoon samples.

Gibbs Plot

The chemical relationships of groundwater based on the lithology of aquifer have been studied following Gibb's [49] plot. Gibbs demonstrated that TDS is plotted on "y" axis, and Na/ (Na$^+$ Ca) in the x axis of cation plot and Cl/(Cl+HCO$_3$) is plotted on "x" axis in the anion plot which would provide information on the mechanism that controls the chemistry of water. The cation and anion plots in both the seasons illustrate that (Figure 5a to d) most of the water samples from fall in the fields of rock-water interaction and evaporation dominance. In the post monsoon, many of the samples fall closer to evaporation field than those of pre-monsoon. The plots indicate that the chemistry of groundwater in majority of the area is influenced by water-rock interaction processes flowed by evaporation.
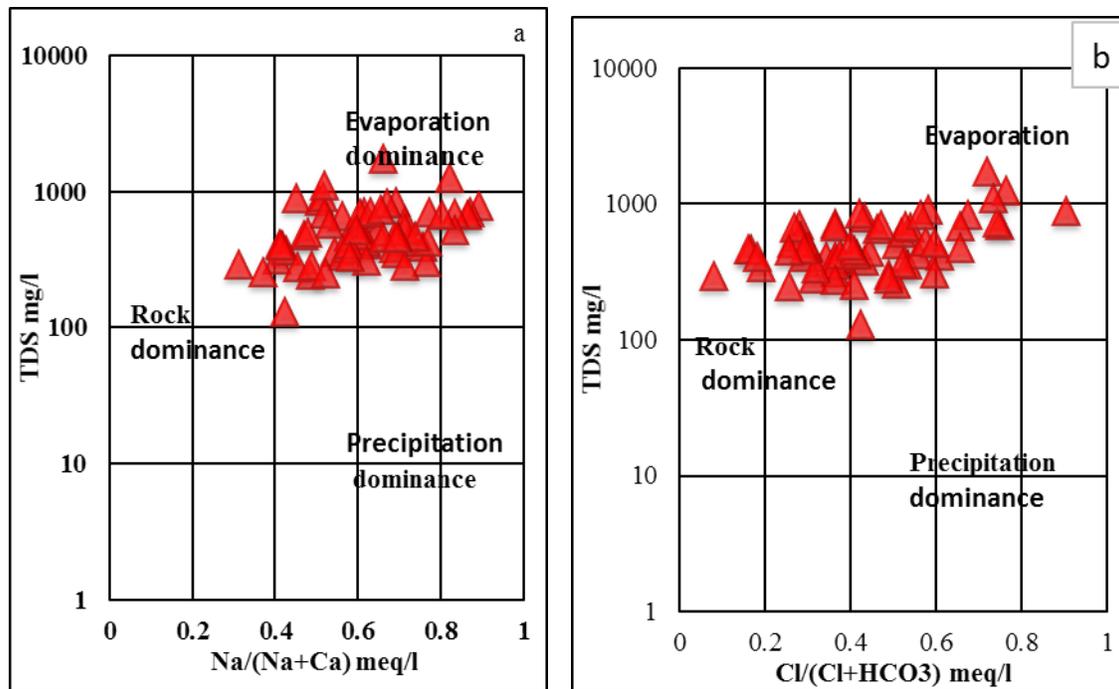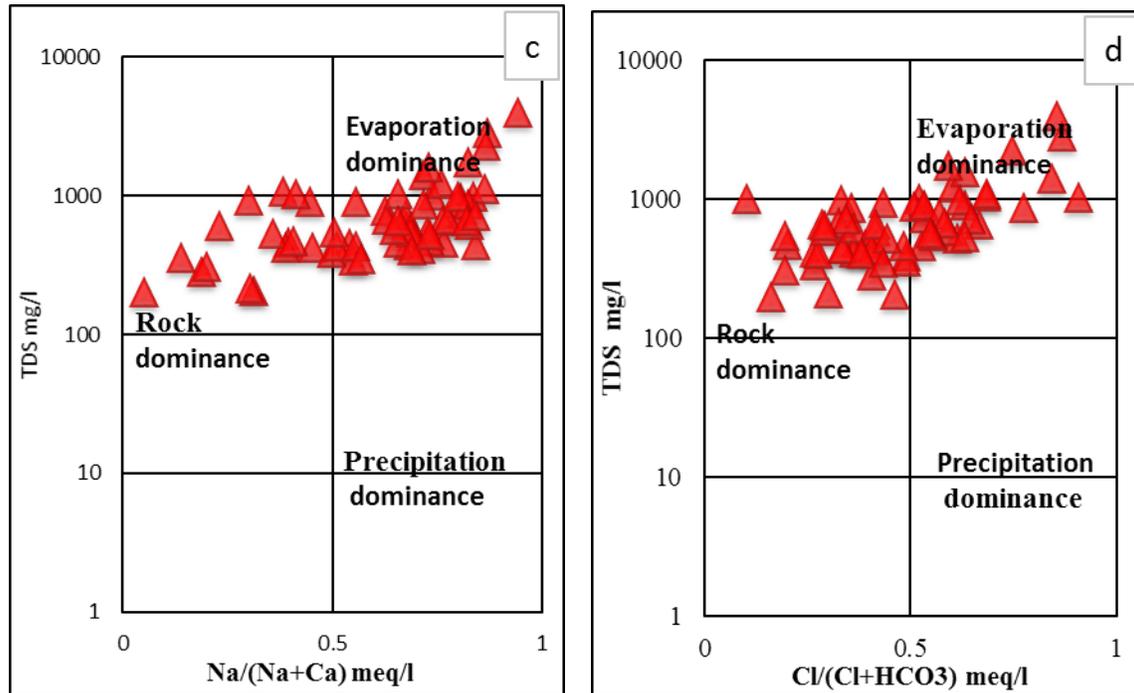
Figures 5 (a-d): Gibbs plot for Pre-monsoon (a,b) and Post-monsoon (c,d) seasons.

Conclusion

The study displayed large temporal, spatial and vertical variations in major ion groundwater chemistry. The stoichiometric analysis reveals the influence of geological (geogenic) conditions more than the anthropogenic activities in increasing concentration of physico-chemical characteristics of groundwater. The predominance of chloride ion in certain areas reflects greater residence time of groundwater. High concentration of bicarbonates in post-monsoon substantiates regular addition of recharge water to aquifers. The factors like slow circulation, longer period of contact between aquifer and water, dissolution of minerals at the time of weathering, drainage pattern and connectivity with surface water are the main factors are responsible for the wide variability in the element concentrations of groundwater.

Ion enrichment in post-monsoon is in contravention of recharge process of rainfall water dilutes the constituents of the groundwater, but infiltrating water also raises the chemical constituents of groundwater due to change in storage by virtue of large-scale recharge-discharge (exploitation and natural base flow). The total dissolved solids as expected are increased along the length of the flow path. In the case of depth variation, it reveals that the shallow aquifer has high concentration of ions as compared to the deeper aquifer. Raise in non-lithogenic ions (HCO_3^-, NO_3^-, Cl^-) in deeper zones in post-monsoon can be accounted for the toxic effluents from different sources are being contaminating the soil and leaching into the groundwater through seepage areas (lineaments). Water-rock interaction stimulated cation exchange

followed by evapotranspiration and direct addition of salt-loaded recharge water could be controlling the water chemistry of this hydrogeologically diverse terrain.

Acknowledgements

References

1. Sengupta S, Sracek O, Jean JS, Lu HY, Wang CH, et al. (2014) Spatial variation of groundwater arsenic distribution in the Chianan Plain, SW Taiwan: Role of local hydrogeological factors and geothermal sources. Journal of Hydrology 518: 393-409.

2. Qiao L, Zhou J, Zhou Y, Bai C, Tao H, et al. (2014) Variation of groundwater hydrochemical characteristics in the plain area of the Tarim Basin, Xinjiang Region, China. Environ Earth Sci 72: 4249-4263.

3. Dhar RK, Zheng Y, Stute M, van Geen A, Cheng Z, et al. (2008) Temporal variability of groundwater chemistry in shallow and deep aquifers of Araihazar, Bangladesh. Journal of Contaminant Hydrology 99: 97-111.

4. Xunhong C, Burbach M, Cheng C (2008) Electrical and hydraulic

vertical variability in channel sediments and its effects on streamflow depletion due to groundwater extraction. Journal of Hydrology 352: 250-266.

5. Netzer L, Weisbrod N, Kurtzman D, Nasser A, Graber ER, et al. (2011) Observations on Vertical Variability in Groundwater Quality: Implications for Aquifer Management. Water Resour Manage 25: 1315-1324.

6. Reddy AGS (2017) Vertical Variation in Groundwater Chemistry of Penna-Chitravathi River Basin in Southern India. Jour Geol Soc India 89: 653-662.

7. Subbarao N (2006) Seasonal variation of groundwater quality in a part of Guntur district, AP, India. Environmental Geology 49: 413-429.

8. Hanson Carl, Phil Abraham (2009) Depth and spatial variation in groundwater chemistry - Central Canterbury Plains. Environment Canterbury Technical Report: Pages 74.

9. Keating EH, Fessenden J, Kanjorski N, Koning DJ, Pawar R (2010) Environ Earth Sci 60: 521.

10. Kura NU, Ramli MF, Sulaiman WNA, Ibrahim S, Aris AZ, Mustapha A (2013) Int. J. Environ. Res. Public Health 10: 1861-1881.

11. Peiyue L, Qian H, Wu J, Zhang Y, Zhang H (2013) Major Ion Chemistry of Shallow Groundwater in the Dongsheng Coalfield, Ordos Basin, China. Mine Water and the Environment 32: 195-206.

12. Narany S, Ramli MF, Aris AZ, Sulaiman WNA, Fakharian K (2014) Spatiotemporal variation of groundwater quality using integrated multivariate statistical and geostatistical approaches in Amol-Babol Plain, Iran. Environ Monit Assess 186: 5797-5815.

13. Kumar SK, Rammohan V, Sahayam JD, Jeevanandam M (2009) Assessment of groundwater quality and hydrogeochemistry of Manimuktha River basin, Tamil Nadu, India. Environmental Monitoring and Assessment 159: 341-351.

14. Nicolas G, Boisson A, Bour O, Maréchal JC (2014) Groundwater flows in weathered crystalline rocks: Impact of piezometric variations and depth-dependent fracture connectivity. Journal of Hydrology 511: 320-334.

15. Singh KP, Gupta S, Mohan D (2014) Evaluating influences of seasonal variations and anthropogenic activities on alluvial groundwater hydrochemistry using ensemble learning approaches. Journal of Hydrology 511: 254-266.

16. Han DM, Song XF, Currell MJ, Yang JL, Xiao GQ (2014) Chemical and isotopic constraints on evolution of groundwater salinization in the coastal plain aquifer of Laizhou Bay, China. Journal of Hydrology 508: 12-27.

17. Peralta-Tapia A, Sponseller RA, Ågren A, Tetzlaff D, Soulsby C, et al. (2015) Scale-dependent groundwater contributions influence patterns of winter baseflow stream chemistry in boreal catchments. J. Geophys. Res. Biogeosci 847-858.

18. Atkinson AP, Cartwright I, Gilfedder BS, Hofmann H, Unland NP, et al. (2015) A multi-tracer approach to quantifying groundwater inflows to an upland river; assessing the influence of variable groundwater chemistry. Hydrological Processes 29: 1-12.

19. Yin S, Wu W, Liu H, Bao Z (2016) The impact of river infiltration on the chemistry of shallow groundwater in a reclaimed water irrigation area. Journal of Contaminant Hydrology 193: 1-9.

20. Lu L, Kashiwaya K, Koike K (2016) Geostatistics-based regional characterization of groundwater chemistry in a sedimentary rock area with faulted setting. Environ Earth Sci 75: 829.

21. Majumder S, Datta S, Nath B, Neidhardt H, Sarkar S, et al. (2016) Monsoonal influence on variation of hydrochemistry and isotopic signatures: Implications for associated arsenic release in groundwater. Journal of Hydrology 535: 407-417.

22. Jessen S, Postma D, Thorling L, Müller S, Leskelä J, et al. (2017) Decadal variations in groundwater quality: A legacy from nitrate leaching and denitrification by pyrite in a sandy aquifer. Water Resources Research 53, 184-198.

23. Statistical Year Book (2013) Directorate of Economics and Statistics, A P, Hyderabad.

24. CGWB (2013) Central Ground Water Board, Brochure, Karimnagar district, Andhra Pradesh. Southern Region Hyderabad.

25. APHA (2012) Standard methods for the examination of water and wastewater, 22nd Edition, ISBN: 9780875530130. Author: E.W. Rice, R.B. Baird, A.D. Eaton, L.S. Clesceri, editors. p1496. American Public Health Association, American Water Works Association, Water Environment Federation.

26. Sarath Prasanth SV, Magesh NS, Jitheshlal KV, Chandrasekar N, Gangadhar K (2012). Evaluation of groundwater quality and its suitability for drinking and agricultural use in the coastal stretch of Alappuzha District, Kerala, India. Applied Water Science 2: 165-175.

27. Davis SN, De Wiest RJM (1966) Hydrogeology. Wiley, NewYork.

28. Freeze RA, Cherry JA (1979) Groundwater. Prentice Hall Inc., New Jersey, p 604.

29. Durfor CN, Becker E (1964) Public water supplies of the 100 largest cities in the United States, 1962. US Geol. Survey Water-Supply Paper 1812: 364.

30. Sawyer GN, McCarthy, DL (1967) Chemistry of sanitary engineers, 2nd edn. Mc Graw Hill, New York, p 518.

31. Soltan ME (1998) Characterization, classification and evaluation of some groundwater samples in Upper Epygt. Chemos 37: 735-747.

32. Soltan ME (1999) Evaluation of groundwater quality in DakhlaOasis (Egyptian Western Desert). Environmental Monitoring and Assessment 57: 157-168.

33. http://www1.agric.gov.ab.ca

34. Buvaneshwari S, Riotte J, Sekhar M, Mohan Kumar MS, Sharma AK, et al. (2017) Groundwater resource vulnerability and spatial variability of nitrate contamination: Insights from high density tube well monitoring in a hard rock aquifer. Science of The Total Environment 579: 838-847.

35. Atkinson AP, Cartwright I, Gilfedder BS, Hofmann H, Unland NP, et al. (2015) A multi-tracer approach to quantifying groundwater inflows to an upland river; assessing the influence of variable groundwater chemistry. Hydrological Processes 29: 1-12.

36. Mahato MK, Singh PK, Tiwari AK (2016) Hydrogeochemical evaluation of groundwater quality and seasonal variation in East Bokaro coalfield region, Jharkhand. Journal of the Geological Society of India 88: 173-184.

37. Han DM, Song XF, Currell MJ, Yang JL, Xiao GQ (2014) Chemical and isotopic constraints on evolution of groundwater salinization in the coastal plain aquifer of Laizhou Bay, China. Journal of Hydrology 508: 12-27.

38. Carl H, Abraham P (2009) Depth and spatial variation in groundwater chemistry - Central Canterbury Plains. Environment Canterbury Technical Report. Report No. R09/39 ISBN 978-1-86937-969-8. www.ecan.govt.nz.

39. Kim K, Rajmohan N, Kim HJ, Hwang GS, Cho MJ (2004) Assessment of groundwater chemistry in a coastal region (Kunsan, Korea) having complex contaminant sources: a stoichiometric approach. Env Geol 46: 763-774.

40. Appelo CAJ, Postma D (2010) Geochemistry, Groundwater and Pollution. 2nd Edition, CRC Press, Boca Raton 32: 649.

41. Ledesma-Ruiz R, Pastén-Zapata E, Parra R, Harter T, Mahlknecht J (2015) Investigation of the geochemical evolution of groundwater under agricultural land: A case study in northeastern Mexico, Journal of Hydrology 521: 410-423.

42. Zang H, Zheng X, Chen J, Qin Z (2015) The impact of hydrogeochemical processes on karst groundwater quality in arid and semiarid area: a case study in the Liulin spring area, north China. Arab J Geosci 8: 6507-6519.

43. Gastmans D, Hutcheon I, Menegário AA, Chang HK (2016) Geochemical evolution of groundwater in a basaltic aquifer based on chemical and stable isotopic data: Case study from the Northeastern portion of Serra Geral Aquifer, São Paulo state (Brazil). Journal of Hydrology 535: 598-611.

44. Ren M, Jones B (2017) Spatial variations in the stoichiometry and geochemistry of Miocene dolomite from Grand Cayman: Implications for the origin of island dolostone. Sedimentary Geology 348: 69-93.

45. Jessen S, Postma D, Thorling L, Müller S, Leskelä J, et al. (2017) Decadal variations in groundwater quality: A legacy from nitrate leaching and denitrification by pyrite in a sandy aquifer. Water Resour. Res 53:184-198.

46. Piper AM (1944) A Graphic Procedure in the Geochemical Interpretation of Water-Analyses. Eos, Transactions American Geophysical Union 25: 914-928.

47. Schoeller H (1967) Qualitative Evaluation of Ground Water Resources. In: Schoeller, H., Ed., Methods and Techniques of Groundwater Investigation and Development. Water Resource Series No. 33, UNESCO, Paris: 44-52.

48. McIntosh JC, Walter LM (2006) Paleowater in Silurian-Devonian carbonate aquifers: Geochemical evolution of groundwater in the Great Lakes region since Late Pleistocene. Geochimica Cosmochimica Acta 70: 2454-2479.

49. Gibbs RJ (1970) Mechanisms controlling World's water chemistry. Science 170: 1088-1090.