International Journal of Chemical Studies

P-ISSN: 2349–8528
E-ISSN: 2321–4902
IJCS 2019; 7(2): 375-380

Received: 13-01-2019
Accepted: 17-02-2019

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Characterization of groundwater quality near industrial estates of Gujarat

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Abstract
A total of 100 groundwater samples were collected in the pre-monsoon and post-monsoon seasons of 2016 from villages in and around Ankleshwar and Panoli industrial estates of Gujarat, India to study the chemistry of ground water. The data obtained were subject to statistical analysis viz. univariate and multivariate. The results indicate that the major hydrochemistry of the study area was NaCl. Cd was beyond the desirable limit for irrigation purpose throughout the year. Correlation studies showed that chlorides and sulphates of Na and Mg had good correlation with electrical conductivity in both the seasons. Five dominant factors explained 63.71% and 58.68% of total variance in pre-monsoon and post-monsoon seasons, respectively. Cluster analysis revealed that cluster A had 42% of sampled sites in pre-monsoon season and 69% in post-monsoon season which were more affected compared to cluster B.

Keywords: groundwater, heavy metal, ions, seasonal variation, PCA, cluster analysis

Introduction
Water is an essential resource for all living organisms in the earth. People in rural area depend on groundwater to meet their demand for domestic and agriculture. Contamination of groundwater due to anthropogenic activities is common in regions where industrialization is on a rise. In order to conserve the groundwater, knowledge of water chemistry influenced by geological and manmade factors need to be understood. Gujarat state of India which is predominantly an industrial state, received 30% less annual rainfall in 2015 compared to decadal average of 2005-2014. The situation was even worse in Bharuch where Ankleshwar and Panoli industrial estates are located. The district received 47% less rainfall in 2015 compared to the said period (CGWB, 2016) [4]. Pollution of groundwater due to industrial effluents is of major concern in regions around these industrial estate since villagers around these estates depend on groundwater for domestic and agriculture purposes. On the other hand, water use has also increased due to increased population growth and rapid industrialization putting tremendous pressure on available groundwater resources. It is clearly evident from various studies that groundwater chemistry is characterized by complex interactions and correlations among a range of variables. Application of different multivariate statistical techniques like correlation analysis, principal analysis and cluster analysis will help in understanding the water chemistry and quality through interpretation of large and complex data sets. This will also allow to better identify the possible chemical parameters influencing the water systems in the study area. Previously multivariate statistical techniques has been used to characterize and evaluate the quality of water due to natural and anthropogenic factors and adopt better management practices for conserving water resources on a local and regional scale (Singh *et al*., 2005 and Shrestha and Kazama, 2007) [10, 11]. In contrast to univariate statistical techniques with simple and reduction process, multivariate techniques better explains a large number of closely related variables without losing much information. Even though multivariate statistical analysis had been used in different regions of India (Kumar *et al*., 2009, Kumar and Riyazuddin, 2008, Singh *et al.*, 2009 and Krishna *et al.*, 2009) [6, 7, 9, 8], little or no such work has been done in the industrially developing regions of Gujarat viz. Ankleshwar and Panoli. Henceforth this work was taken up to study the chemistry of groundwater and the possible cause for groundwater pollution in these regions.

Materials and Methods

100 groundwater samples were collected from tube wells ranging in depth from 35-250 feet during pre-monsoon (April - 2016) and post-monsoon (December - 2016). The sampling sites were from villages in and around Ankleshwar and Panoli GIDC between 21°40′39.4″ and 21°31′54.6″ North latitude and 73°03′31.1″ to 72°48′44.3″ East Longitude covering an area of 648 sq.km (Fig. 1). Collected samples were analysed for major ions and heavy metals. For heavy metal analysis samples were collected in acid leached polyethylene bottles after running the well for about 5 minutes and preserved by adding 2ml of nitric acid for 1 litre of collected sample.

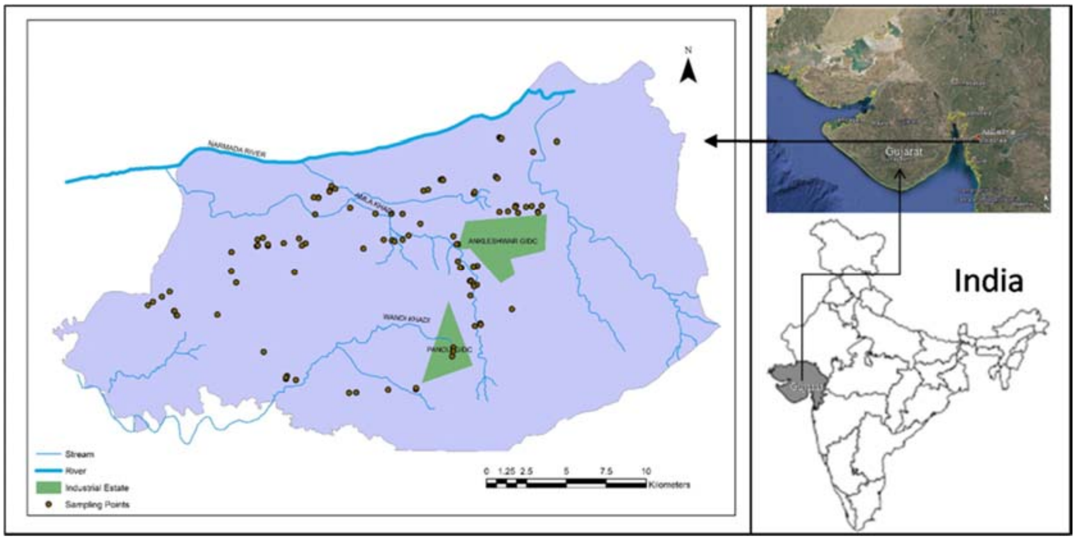


Fig 1: Location map of the study area

19 parameters were analysed using the recommended standard procedures. pH and electrical conductivity with pH meter and conductivity meter, respectively (APHA, 2005) [1]. Sodium and potassium were analysed using flame photometer (Barnes *et al.,* 1945) [2]. Calcium and magnesium by titration with EDTA, chloride by titration with $AgNo_3$, sulphate by turbidimetric method and carbonates and bicarbonates by titration with H_2So_4 (APHA, 2005) [1]. Heavy metals like cadmium, cobalt, copper, iron, manganese, nickel, lead and zinc by atomic absorption spectrometry (Burrell, 1975) [3]. The water quality datas thus obtained were subjected to both univariate analysis: range, mean, standard deviation, skewness and kurtosis and multivariate analysis: correlation, principal component analysis (PCA) and cluster analysis (CA). Statistical computations were done using the statistical software package, SPSS version 23.0.

Results and Discussion

Descriptive statistics

Univariate overview of groundwater chemistry in the study area for pre-monsoon and post-monsoon seasons is presented in Table. 1. The pH of groundwater in both the seasons were neutral to mildly alkaline and conductivity varied from 0.28 to 11.40 dS/m and 0.30 to 9.30 dS/m in pre-monsoon and post-monsoon, respectively. In pre-monsoon season, mean cationic concentrations occurred in the order of Na > Mg > Ca > K > Zn > Ni > Pb > Mn > Cu > Fe > Cr > Co > Cd and anions in the order of Cl > Co3 > So4 > HCo3. Chloride is the predominant anion in both pre-monsoon and post-monsoon seasons whose concentrations ranged from 178 to 2929 mg/l in pre-monsoon and 53 to 3639 mg/l in post-monsoon. High concentration of chloride may be due to geological factors and seepage from industrial effluents (Gulgundi and Shetty, 2018) [5]. In post-monsoon season, anions were in the same order as that of pre-monsoon. However abundance of cations were in the order of Na > Mg > Ca > K > Fe > Zn > Pb > Mn > Cu > Ni >Cd. The values of Na, K, Ca, Mg, Fe, Cl, So4 and HCo3 got enhanced in post-monsoon season and the values of Co3, Cd, Cu, Mn, Ni, Pb and Zn reduced. Mean concentrations of all the parameters were below the prescribed desirable limits for irrigation water in both the seasons except for Cd. In pre-monsoon season, heavy metals like Cd (49% of sampled sites), Co (43%), Ni (31%), Cr (27%) and Mn (19%) in groundwater were beyond desirable limit for irrigation purpose whereas in post-monsoon season only Cd (59%) exceeded the limit (Table. 2). Based on US Salinity Laboratory diagram (Fig. 2) for irrigation water quality majority of samples, 32% and 38% in pre-monsoon and post-monsoon, respectively fall in C3-S1 (high salinity with low sodium) category, followed 23% and 20% in C3-S2 (high salinity with medium sodium). 10% of samples in pre-monsoon

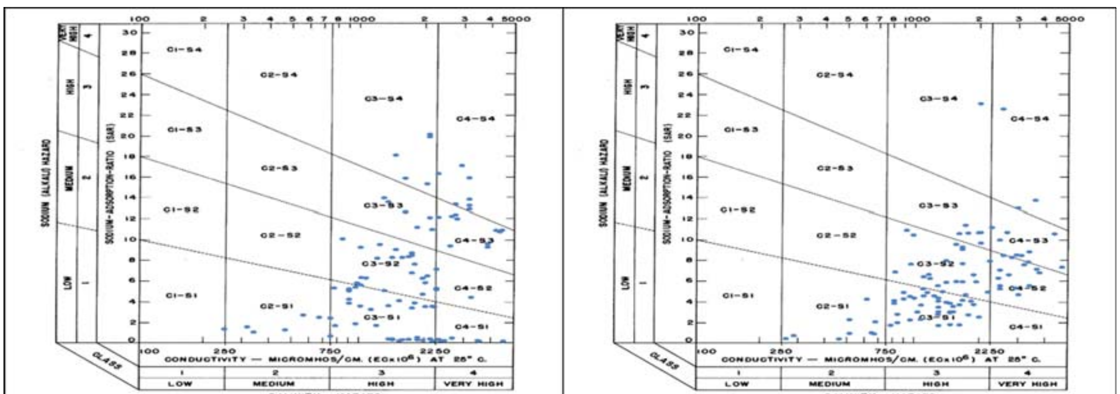
Table 1: Descriptive statistics (range, mean, standard deviation, skewness, kurtosis) of groundwater in pre- and post-monsoon season.

	Units	Season	Range	Mean	Std. deviation	Skewness	Kurtosis
EC	dS/m	Pre-monsoon	0.28 -11.40	3.20	2.02	1.35	2.45
		Post-monsoon	0.30 -9.30	2.90	1.82	1.17	1.26
pH	-	Pre-monsoon	6.76 -8.28	7.50	0.31	0.23	-0.41
		Post-monsoon	6.78 -8.12	7.40	0.31	0.24	-0.52
K	mg/l	Pre-monsoon	1.00 -448.00	17.50	48.41	7.65	65.25
		Post-monsoon	1.00 -535.00	24.50	65.19	6.04	41.45
Na	mg/l	Pre-monsoon	10.00 -1651.00	360.80	334.97	1.09	1.07
		Post-monsoon	24.00 -1407.00	401.60	272.39	1.16	1.28

Ca	mg/l	Pre-monsoon	20.00 - 210.00	86.50	44.25	0.86	0.24
		Post-monsoon	20.00 - 440.00	95.40	63.40	2.37	8.52
Mg	mg/l	Pre-monsoon	0.00 - 632.00	171.10	140.88	1.01	0.80
		Post-monsoon	0.00 - 729.00	173.20	151.47	1.25	1.48
Cl	mg/l	Pre-monsoon	178.00 - 2929.00	765.00	514.69	1.65	3.08
		Post-monsoon	53.00 - 3639.00	1004.70	603.49	1.73	3.96
SO_4	mg/l	Pre-monsoon	10.00 - 595.00	179.00	155.25	1.18	0.57
		Post-monsoon	0.00 - 671.00	185.30	155.98	1.27	1.06
CO_3	mg/l	Pre-monsoon	150.00 - 1050.00	430.50	174.06	0.62	0.83
		Post-monsoon	0.00 - 780.00	370.50	136.94	-0.21	0.99
HCO_3	mg/l	Pre-monsoon	0.00 - 610.00	32.00	109.01	3.90	16.03
		Post-monsoon	0.00 - 671.00	65.60	145.81	2.46	5.44
Cd	mg/l	Pre-monsoon	0.00 - 1.81	0.03	0.18	9.95	99.26
		Post-monsoon	0.00-0.02	0.01	0.01	-0.38	-1.87
Co	mg/l	Pre-monsoon	0.00 - 0.12	0.05	0.03	0.28	-0.70
		Post-monsoon	-				
Cr	mg/l	Pre-monsoon	0.00 - 0.23	0.06	0.06	0.28	-1.08
		Post-monsoon	-				
Cu	mg/l	Pre-monsoon	0.00 - 0.25	0.09	0.04	0.98	2.18
		Post-monsoon	0.00 - 0.04	0.02	0.01	0.11	-0.40
Fe	mg/l	Pre-monsoon	0.00 - 0.65	0.08	0.12	2.69	7.99
		Post-monsoon	0.06 - 0.27	0.10	0.04	1.52	2.24
Mn	mg/l	Pre-monsoon	0.00 - 0.88	0.10	0.17	2.28	5.44
		Post-monsoon	0.00 - 0.42	0.02	0.05	6.15	42.34
Ni	mg/l	Pre-monsoon	0.03 - 0.35	0.17	0.06	0.19	-0.32
		Post-monsoon	0.00 - 0.09	0.01	0.02	2.74	6.38
Pb	mg/l	Pre-monsoon	0.00 - 0.53	0.16	0.16	0.47	-1.08
		Post-monsoon	0.00 - 0.04	0.02	0.01	-0.12	-0.16
Zn	mg/l	Pre-monsoon	0.01 - 2.92	0.18	0.43	4.72	24.31
		Post-monsoon	0.01 - 1.42	0.07	0.21	5.52	32.04

Table 2: Percentage of sampled sites beyond the prescribed desirable limit for irrigation (n=100)

Heavy metals	Pre-monsoon	Post-monsoon
Cd	49	59
Co	43	-
Cr	27	-
Cu	1	0
Fe	0	0
Mn	19	2
Ni	31	0
Pb	0	0
Zn	2	0



Pre-monsoon (2016) | Post-monsoon (2016)

Fig 2: Wilcox graph for irrigation water quality classification

and 15% of samples in post-monsoon fall in C4-S3 (very high salinity with high sodium) and C4-S2 (very high salinity with medium sodium) categories, respectively.

Correlation analysis

The correlation matrixes prepared for pre-monsoon season (Table. 3a) and post-monsoon season (Table. 3b) with 19 variables clearly illustrate that electrical conductivity (EC) had a good positive correlation with cations like Mg (0.76 and 0.75, pre-monsoon and post-monsoon, respectively) and Na (0.64 and 0.85) and anions like Cl (0.93 and 0.90) and So4 (0.75 and 0.85). Na and Mg also exhibited positive correlation with both Cl and So4 in both pre-monsoon and post-monsoon seasons. Co-Cu, Co-Ni, Co-Pb, Cr-Cu, Cr-Pb and Cu-Pb had more significant correlation pairs among heavy metals in pre-monsoon season. In post-monsoon season there was no significant correlation among heavy metal variables in the matrixes.

Table 3a: Correlation matrix for groundwater in pre-monsoon season.

	EC	**pH**	**K**	**Na**	**Ca**	**Mg**	**Cl**	**SO_4**	**CO_3**	**HCO_3**	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
EC	1.00																		
pH	-0.57	1.00																	
K	0.18	-0.21	1.00																
Na	0.64	-0.27	-0.03	1.00															
Ca	0.56	-0.44	0.23	0.27	1.00														
Mg	0.76	-0.59	0.22	0.49	0.48	1.00													
Cl	0.93	-0.46	0.08	0.71	0.57	0.75	1.00												
SO_4	0.75	-0.48	0.03	0.69	0.50	0.72	0.78	1.00											
CO_3	-0.05	-0.07	-0.07	0.06	-0.02	-0.04	0.00	0.08	1.00										
HCO_3	-0.08	0.14	-0.02	-0.03	-0.12	-0.06	-0.11	-0.03	-0.37	1.00									
Cd	-0.09	0.07	-0.03	-0.05	0.11	-0.07	-0.08	-0.08	0.02	-0.03	1.00								
Co	0.67	-0.64	0.22	0.45	0.52	0.83	0.67	0.67	0.03	-0.05	0.03	1.00							
Cr	0.32	-0.26	-0.13	0.58	0.22	0.40	0.41	0.52	0.09	-0.06	0.10	0.60	1.00						
Cu	0.37	-0.30	0.01	0.37	0.34	0.52	0.43	0.46	0.00	-0.07	0.02	0.70	0.65	1.00					
Fe	0.05	0.00	-0.06	0.12	-0.01	0.15	0.11	0.04	0.01	0.14	-0.05	0.21	0.24	0.29	1.00				
Mn	-0.04	-0.10	0.03	-0.06	0.06	0.20	-0.01	0.02	0.20	-0.05	0.02	0.35	0.26	0.45	0.37	1.00			
Ni	0.22	-0.35	0.23	0.03	0.15	0.34	0.11	0.10	-0.07	0.12	0.12	0.63	0.33	0.48	0.09	0.32	1.00		
Pb	0.35	-0.31	-0.10	0.57	0.30	0.46	0.46	0.56	0.11	-0.11	0.10	0.69	0.97	0.74	0.23	0.33	0.37	1.00	
Zn	0.11	-0.05	0.03	0.03	0.07	0.19	0.08	0.19	0.00	0.11	-0.02	0.12	0.00	0.00	0.22	0.00	-0.04	-0.01	1.00

Table 3b: Correlation matrix for groundwater in post-monsoon season.

	EC	pH	K	Na	Ca	Mg	Cl	SO_4	CO_3	HCO_3	Cd	Cu	Fe	Mn	Ni	Pb	Zn
EC	1.00																
pH	-0.17	1.00															
K	0.02	0.16	1.00														
Na	**0.85**	0.00	-0.10	1.00													
Ca	**0.68**	-0.27	0.07	0.56	1.00												
Mg	**0.75**	-0.34	0.08	0.48	0.50	1.00											
Cl	**0.90**	-0.23	-0.01	**0.73**	0.59	**0.70**	1.00										
SO_4	**0.85**	-0.25	-0.03	**0.74**	0.57	0.54	**0.76**	1.00									
CO_3	-0.09	0.11	0.09	-0.07	-0.12	-0.03	-0.13	-0.18	1.00								
HCO_3	0.08	0.15	0.26	0.07	0.03	0.05	0.08	0.04	-0.54	1.00							
Cd	-0.07	0.03	0.05	-0.06	0.02	-0.09	-0.02	-0.01	-0.05	0.05	1.00						
Cu	-0.11	-0.11	-0.04	-0.15	-0.04	-0.07	-0.08	-0.03	-0.06	0.06	-0.12	1.00					
Fe	-0.07	-0.19	-0.19	-0.07	-0.11	-0.18	-0.01	0.12	-0.08	-0.14	-0.27	0.33	1.00				
Mn	0.16	-0.23	0.03	0.00	0.35	0.23	0.16	0.12	0.15	-0.12	0.00	0.12	0.05	1.00			
Ni	0.13	-0.03	0.11	0.01	0.14	0.01	0.01	0.19	-0.04	0.15	-0.35	0.39	0.10	-0.09	1.00		
Pb	-0.01	-0.35	0.05	-0.21	0.08	-0.02	0.03	0.13	-0.13	-0.02	-0.08	0.16	0.32	0.05	0.26	1.00	
Zn	-0.09	0.12	-0.09	-0.07	-0.09	-0.19	-0.09	0.02	0.03	0.01	0.07	0.22	0.35	-0.05	-0.08	0.07	1.00

Principal Component Analysis (PCA)

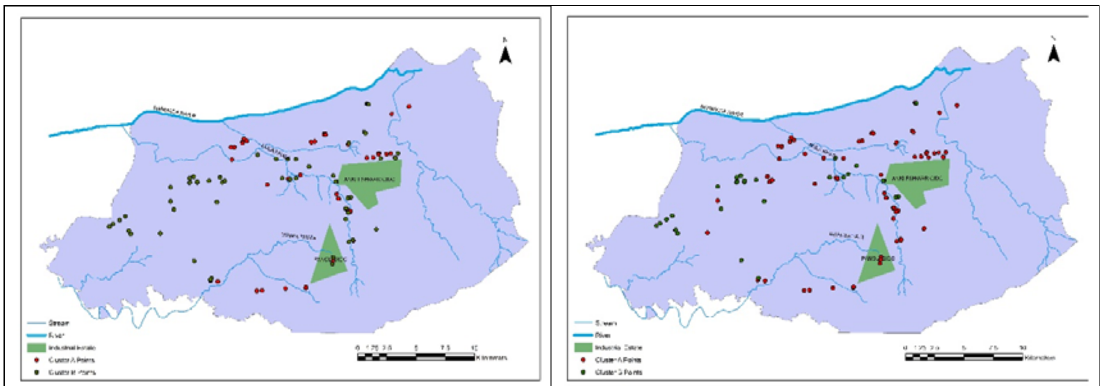
The final output of varimax rotated principal component analysis indicates that four principal components explain 63.79% and 58.68% of the total variance in in pre-monsoon and post-monsoon seasons, respectively (Table. 4). Principal Component – I (PC-I), PC-II, PC-III and PC-IV contributed to 35.71%, 11.56%, 8.76% and 7.76% of the total variation in pre-monsoon season with 16 variables. In post-monsoon season, PC-I, PC-II, PC-III and PC-IV contributed to 27.22%, 12.89%, 10.19% and 8.37% of the total variation with 14 variables. PC-I was dominated by EC, Na, Ca, Mg, Cl and So_4 with high positive loadings of 0.597-0.811 in pre-monsoon season and 0.741-0.979 in post-monsoon season. There was strong negative loading of pH (-0.628) in pre-monsoon season. Heavy metals like Co, Cr, Cu and Pb dominated PC-I in the pre-monsoon season (0.707-0.916). In post-monsoon season they were absent. PC-II had higher positive loadings of Mn in pre-monsoon season (0.656) and post-monsoon season (0.432). In addition to Mn, post-monsoon season also had strong positive loading of Pb (0.674) and negative loading of pH (-0.813). PC-III was dominated by K and Ni in pre-monsoon season and Co_3 and HCo_3 in post-monsoon season. PC-IV had high positive loadings of Co_3 and HCo_3 in pre-monsoon season and heavy metals like Cu, Fe and Zn in post-monsoon season.

Cluster Analysis (CA)

The results of cluster analysis established that the sampled sites were principally divided into two large clusters (A and B) in both pre-monsoon and post-monsoon seasons. The sites under each clusters with site id are presented in Table 5 and Fig. 3. In both the clusters in both the seasons, the major hydrochemistry was NaCl and the concentration of cations and anions were in the order of Na>Mg>Ca>K and Cl>Co_3>So_4>HCo_3, respectively. In case of heavy metals, cluster A in pre-monsoon season had concentrations of Cd and Cr beyond the desirable limit prescribed for irrigation purpose. But in post-monsoon season all the heavy levels were under desirable limit except for Cd. In cluster B, all the heavy metals were under prescribed desirable levels in both the seasons except for Cd in pre-monsoon season. It is conclusive that Na, Cl, Cr and Cd are the major parameters in cluster A affecting water quality in the pre-monsoon season. It is clearly evident from Fig. 3 that sampling points near the industrial estates and khadis where the effluents are discharged have poor water quality compared to sampling points away from these areas in both the seasons. The percentage of sites under cluster A increased from 42 in pre-monsoon season to 69 in the post-monsoon season.

Table 4: Varimax rotated principal component loadings explaining 70.36% and 66.50% of total variance in pre-monsoon and post-monsoon season for groundwater

Parameters	Varifactors (Pre-monsoon)				Varifactors (Post-monsoon)			
	VF1	VF2	VF3	VF4	VF1	VF2	VF3	VF4
EC	.811	-.461	.017	.041	.979	-.020	.027	-.050
pH	-.628	.209	-.282	.254	-.208	-.813	.046	.105
K	.142	-.236	.636	-.209	-.014	-.091	.067	-.089
Na	.689	-.180	-.454	.173	.870	-.285	.041	-.026
Ca	.597	-.287	.165	-.185	.741	.232	-.033	-.041
Mg	.846	-.191	.189	.039	.747	.186	-.063	-.249
Cl	.835	-.389	-.152	.067	.909	.065	.053	-.027
SO_4	.825	-.280	-.221	.089	.871	.092	.101	.132
CO_3	.053	.163	-.343	-.587	-.097	-.209	-.860	-.011
HCO_3	-.098	.045	.275	.750	.062	-.120	.802	.013
Cd	-.006	.214	.025	-.197	-.044	.005	.141	.034
Co	.916	.127	.258	-.049	-	-	-	-
Cr	.707	.454	-.342	.064	-	-	-	-
Cu	.724	.452	.040	.026	-.098	.247	.030	.553
Fe	.216	.430	.018	.415	-.043	.296	-.029	.647
Mn	.266	.656	.221	-.136	.217	.432	-.425	.096
Ni	.438	.401	.569	-.074	.071	.102	.144	.090
Pb	.766	.463	-.285	.006	-.049	.674	.145	.186
Zn	.120	-.107	.087	.369	-.045	-.157	.000	.844
Eigen Values	6.79	2.20	1.67	1.47	4.63	2.19	1.73	1.42
% of total variance	35.71	11.56	8.76	7.76	27.22	12.89	10.19	8.37
Cumulative% variance	35.71	47.27	56.03	63.79	27.22	40.11	50.31	58.68



Pre-monsoon (2016) | Post-monsoon (2016)

Fig 3: A graphic representation of the study area highlighting the clusters – A and B for pre-monsoon and post-monsoon seasons of 2016.

Table 5: Mean values for all chemical constituents for each cluster (all units in mg/l except for EC and pH)

Parameters	Pre-monsoon		Post-monsoon	
	Cluster A	Cluster B	Cluster A	Cluster B
EC	4.31	2.47	3.38	1.85
pH	7.34	7.53	7.33	7.63
K	14.49	19.73	30.57	11.11
Na	583.09	199.77	471.79	245.44
Ca	98.10	78.10	103.77	76.77
Mg	258.44	107.93	192.14	130.96
Cl	1094.58	526.38	1130.60	724.31
SO_4	282.60	103.96	220.04	107.87
CO_3	450.00	416.38	373.91	362.90
HCO_3	18.15	42.07	86.64	18.69
Cd	0.02	0.04	0.02	0.00
Co	0.07	0.03	-	-
Cr	0.11	0.03	-	-
Cu	0.12	0.07	0.02	0.01
Fe	0.13	0.05	0.10	0.11

Mn	0.18	0.05	0.02	0.01
Ni	0.19	0.16	0.01	0.00
Pb	0.30	0.06	0.02	0.00
Zn	0.14	0.20	0.06	0.00
Major hydrochemistry	NaCl	NaCl	NaCl	NaCl
Sites	1-3, 6-8, 13, 15-19, 21-23, 27-31, 34-41, 45, 49, 50, 52, 54-60, 78-80	4, 5, 9-12, 14, 20, 24-26, 32, 33, 42-44, 46-48, 51, 53, 61-77, 81-100	1-60, 62, 66, 72, 75, 79, 80, 84, 94, 98	61, 63-65, 67-71, 73, 74, 76-78, 81-83, 85-93, 95-97, 99, 100
% sites	42	58	69	31

Conclusion

Correlation analysis of 19 parameters of groundwater revealed that electrical conductivity had positively high correlation with Na, Mg, Cl and So4 in both the seasons indicating that the salts were mainly of chlorides and sulphates of Na and Mg. Four varimax factors accounted for 63.79% and 58.68% of total variance in pre-monsoon and post-monsoon seasons, respectively. The first factor – salinization – explained 35.71% of total variance in pre-monsoon and 27.22% of total variance in post-monsoon. Cluster analysis resulted in two main clusters with NaCl as major hydrochemistry but at varying intensities. Cluster A had high concentrations of NaCl compared to B. Cluster A also had heavy metals like Cd and Cr beyond desirable limit for irrigation. The results clearly demonstrates that compared to univariate statistical analysis, multivariate is a useful tool for understanding the chemistry of groundwater in the study area.

Acknowledgement

This research was supported by Indian Council for Agricultural Research under “Agri-Consortia Research Platform on Water” vide letter No. NRM-10(12)/2015-SW&DF Dt. 17.12.2015.

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