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GROUNDWATER QUALITY INDEX, STATISTICAL CORRELATION, SEASONAL AND ANNUAL COMPARATIVE HYDROCHEMICAL ANALYSIS OF ATHGARH BASIN, INDIA: AN INTEGRATED EMPIRICAL STUDY

ROSALIN DAS

PG Department of Geology, Fakir Mohan University, Balasore, Odisha, India

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ABSTRACT

This study aimed to explore and understand groundwater hydrochemistry, evaluate the groundwater quality of the Athgarh basin comprehensively using Water Quality Index (WQI) and statistical correlations. Accordingly, the quality of the groundwater was assessed for drinking purposes. Moreover, seasonal variation and annual variation of water quality have been monitored for two consecutive years after systematic collection of groundwater samples and their methodical physico-chemical analysis. For calculating the WQI, 13 parameters (viz., pH, EC, total dissolved solids, total hardness, calcium, sodium, potassium, magnesium, bicarbonate, chloride, fluoride, sulphate and nitrate) have been considered. The analyzed value is compared with the prescribed limits of WHO for drinking suitability. Hydrological facies were evaluated through Piper's trilinear diagram and Chadha's diagram using cation and anion values. A systematic statistical correlation study deciphers the significant linear relationship among different pairs of water quality parameters.

KEY WORDS : Water Quality Index, Geochemical facies, Correlation Coefficient, Athgarh Basin

INTRODUCTION

Efficient management of water resources requires information about water quality and its variability. The study area, Athgarh Basin of Athgarh Formation covering an area of 800 sq. km forms an important stratigraphic unit of a thick pile of fresh water and lacustrine sediments known as Upper Gondwana in Indian stratigraphy. Geographically the area is situated between latitude 20°152 and 20°332 N and longitudes 85°352 and 85° 502 E (Fig. 1). It features in survey of India toposheet No. 73H/10, 73H/11, 73H/12, 73H/13, 73H/14, 73H/15, 73H/16 in (1 cm=0.64 km). On the North West, the Athgarh Formation rests unconformably on the Pre-cambrian basement rocks of the Eastern Ghats Group with a faulted contact (Raja Rao and Mitra, 1978). In the east, it is covered by sub-recent and recent alluvial tract, which is built up by the river Mahanadi. The Athgarh succession shows a regular change in lithologic characteristics from the basin margin towards the basin center (Fig. 2) i.e., from northwest to southeast. Mahanadi River forms the main drainage artery of the Athgarh Basin. The regional slope and the geomorphic features control the drainage of the area. Lithologically the area covers with 65% sandstone, 10% mudstone, shale, patchy occurrences of laterite and dolomite and fireclay deposits. The hydro-chemical parameters of the ground water of the study area are compared with the prescribed specification recommended by the World Health Organization (WHO, 2004) and the Indian standard for drinking water IS-10500:1991 (BIS, 2012) for assessing the quality of water for public health purpose. Monitoring and controlling surface water are necessary and vital to assure the availability of high-quality water for its many uses (Sánchez *et al.,* 2007). One of the simple methods that can recount the qualitative conditions of water is the use of water quality indices (Hoseinzadeh *et al.,* 2015; Barakat *et al.,* 2018). The Water Quality Index (WQI) was designed by Horton (1965), Brown *et al.* (1972) and has been further developed by various researchers (Wang *et al*., 2017; Wang *et al.,* 2018). This index helps in making qualitative classification of surface water. With its implementation, it is likely to produce an appropriate view regarding water quality (Sánchez *et al.,* 2007). Although various formulae are available to calculate the WQI, all of them effectively convert numerous physical and chemical parameters into a single value that reflects the water quality level, thus eliminating differences between the parameters used individually in the assessment. The WQI method has been widely applied to evaluate both surface water and groundwater quality. The correlation provides an excellent tool for the prediction of parametric values within a reasonable degree of accuracy (Venkatachalam and Jabenesan, 1998). The quality of water is described by its physical, chemical and microbial characteristics. Possible correlations among these parameters are useful in assessing the overall quality of water (Dhembare and Pondhe, 1997). It also helps in quantifying the relative concentration of various pollutants in water and provides a necessary cue for the implementation of rapid water quality management programs (Dash *et al.,* 2006). The location of the study area is shown in (Fig. 1).

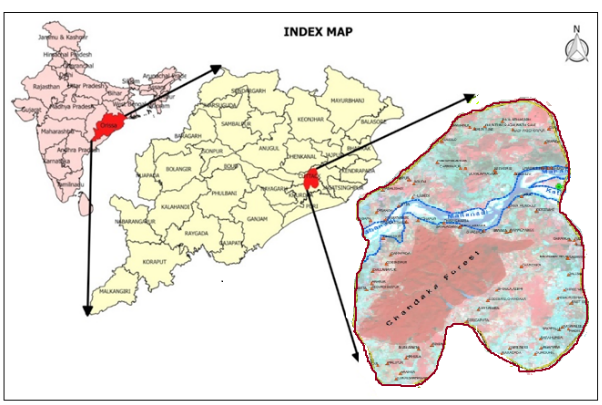

Fig. 1. Location Map of the study area showing sampling sites

MATERIALS AND METHODS

The quality of groundwater is highly influenced by the lithology, chemical composition of the aquifer and climatic conditions prevailing during the formation. Therefore, the chemical analysis of groundwater samples provides direct information about the present quality of the aquifer. The study involves the assessment of water quality of the basin and analyzed the major contaminants based on the WQI. Sampling was conducted at 75 sampling sites from different groundwater abstraction structures e.g., tube wells, dug wells spreading over the entire Athagarh Basin three times a year and monitored for two consecutive years i.e., 2015-16 and 2016-17 (Fig. 2). Out of 75 samples, 65 samples are collected from tube wells (slotted with PVC well casing pipe) and 10 samples from dug wells (7 from sandstone, 2 from alluvium and 1 from laterite). The depths of water table of dug wells are generally within 11 to 20 ft, whereas the depths at Mahakalabasta (Sandstone) and Ilukrishnanagar (Laterite) are 37 ft and 4 ft respectively. A comprehensive analysis of pH, electrical conductivity, total dissolved solids, total alkalinity, total hardness, calcium, magnesium, sodium, potassium, bicarbonate, carbonate, chloride, fluoride, sulphate and nitrate were undertaken by standard analytical procedures used for analysis of water and wastewater (APHA, 1992). Special care was taken to avoid the error. Each water sample was taken for analysis by using a double beam spectrophotometer, flame photometer, water analyzer, etc.

Water Quality Index

WQI, indicating the water quality in terms of an index number, offers a useful representation of the

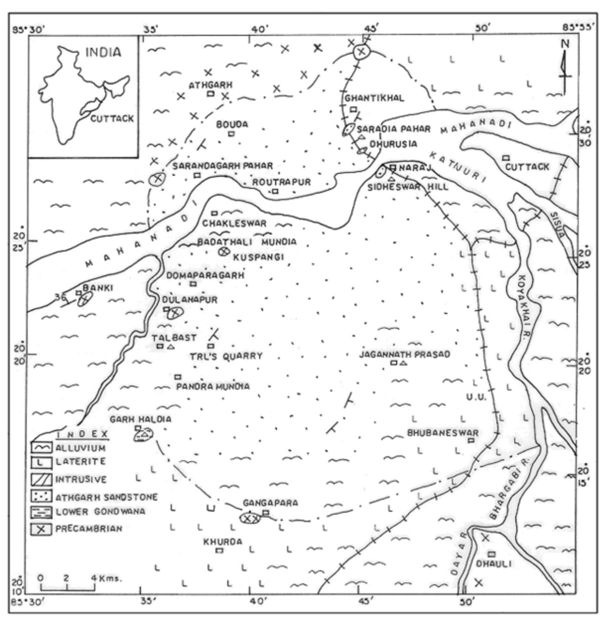

Fig. 2. Geological Map of Athgarh Basin, Odisha, India. (After Patra and Sahoo, 1996)

overall quality of water for public use or any intended use. The index assigns a number to a body of water and its sign of quality. The Horton model of water quality index contains four standards of WQI components, i.e., parameter selection, parameter weighing, sub-index calculation and sub-index aggregation. WQI is computed following standard analytical procedure given by Horton (1965).

For this, thirteen physico chemical parameters were taken in to consideration such as hydrogen ion concentration, electrical conductivity, total dissolved solids, total alkalinity, total hardness, calcium, magnesium, sodium, potassium, bicarbonate, carbonate, chloride, fluoride, sulphate and nitrate.

Depending on environmental impact and relative influence in overall quality of water, each of the thirteen parameters has been assigned a weight value (wi) between 1 to 5 as presented in Table 1. The maximum weight of 5 assigned to nitrate; weight value 4 assigned to 5 parameters (hydrogen ion concentration, electrical conductivity, total hardness, sulphate and fluoride); the weight value 3 assigned to bicarbonate, chloride and sodium; 2 assigned to 4 parameters (calcium, magnesium, potassium and total dissolve solids) (Mufid, 2012).

The relative weight (Wi) is computed using the following weighted arithmetic index method.

$Wi = wi/(\sum_{i=1}^{n} wi)$, where, Wi is the relative weight, wi is the weight of each parameter and n is the number of parameters (Brown *et al.*, 1972; Horton, 1965).

A quality rating scale (Qi) for each parameter is assigned by dividing its concentration in each water sample by its respective standard according to the guidelines (APHA, 2005) and then multiplied by 100,

$Qi = \left(\frac{Ci}{Si}\right) * 100$, where, Qi is the quality rating, Ci is the concentration of chemical parameter of each water sample and Si is the drinking water standard for each chemical parameter.

The Sub-index values (SI) are determined for each chemical parameter for calculation of WQI, as per the following equation.

$SIi = Wi \times Qi$, where, SIi is the sub-index of the ith parameter and Qi is the rating based on the concentration of the ith parameter.

The overall Water Quality Index (WQI) is calculated by sub-index aggregation as follows:

$$WQI = \sum SIi$$

Water Quality Indices for all the sampling locations are calculated for pre-monsoon, monsoon and post-monsoon of (2015-2016) and (2016-2017). Accordingly, computed WQI values are classified into five categories (Table 2).

Statistical analysis

The statistical analysis helps in the interpretation of groundwater quality data and relating them to specific hydro-geological processes. These tools are quite useful for the identification of the distribution patterns of different water quality parameters in groundwater samples. The physico-chemical parameters of the investigated area were explored by calculating Pearson's correlation coefficient (r) value in order to assess the relationship between water quality variables. With the purpose of calculation of correlation coefficients, a correlation matrix was constructed by calculating the

Table 1. Weight and Relative Weight for Each Parameter (Mufid, 2012)

Sr. No	Chemical Parameter	Standard	Weight (wi)	Relative Weight (Wi)
1.	pH	8.5	4	0.095238095
2.	EC	750	4	0.095238095
3.	TDS	500	2	0.047619048
4.	TH	300	4	0.095238095
5.	Ca	75	2	0.047619048
6.	Mg	30	2	0.047619048
7.	Na	200	3	0.071428571
8.	K	12	2	0.047619048
9.	HCO_3	250	3	0.071428571
10.	Cl	250	3	0.071428571
11.	F	1	4	0.095238095
12.	SO_4	200	4	0.095238095
13.	NO_3	45	5	0.119047619
			Σwi = 42	ΣWi = 1

Table 2. WQI ranges, status, and possible use of the water sample for the year 2015-2017 (pre-monsoon, monsoon & post-monsoon) (Brown *et al.*, 1972)

Sr. No.	WQI range	Type of Water	2015-2016 (% of samples)			2016-2017 (%of samples)			Possible Use
			Pre monsoon	Monsoon	Post monsoon	Pre monsoon	Monsoon	Post monsoon	
1	1 < 50	Excellent	74.6%	69.3%	66.7%	77.3%	60%	61.3%	Drinking, irrigation, and industrial
2	50.1 – 100	Good	22.6%	25.3%	33.3%	22.6%	40%	38.6%	Drinking, irrigation, and industrial
3	100.1 – 200	Poor							Irrigation and industrial
4	200.1 – 300	Very Poor							Irrigation
5	> 300.1	Unfit for Drinking		2.6%					Proper treatment required before use

coefficients of different pairs of parameters depicted in (Tables 3-8). A correlation coefficient near -1 or 1 means the strongest negative or positive relationship between them. The following formula is used to calculate the Pearson's correlation coefficient (r):

Karl Pearson's Coefficient of Correlation $$r = \frac{n\sum xy - \sum x \sum y}{\sqrt{n\sum x^2 - \left(\sum x\right)^2}\sqrt{n\sum y^2 - \left(\sum y\right)^2}}$$

Where, r = Pearson correlation coefficient, N = number of values in each data set, “xy = sum of the products of paired scores, “x = sum of x scores, “y = sum of y scores, “x^2= sum of squared x scores, “y^2= sum of squared y scores.

RESULTS AND DISCUSSION

The quality of drinking water is as important as quantity and hence the quality should be studied as most of the diseases are due to the poor quality of water. To assess the suitability of water for public health purpose, the hydro-chemical parameters of the surface and subsurface water of the study area are compared (Das *et al.*, 2012, 2013) with the prescribed specifications recommended by World Health Origination (WHO, 2004) and Indian standard for drinking water IS-10500 (BIS, 2012) (Table 9). This comparison reflects the seasonal and annual variations of groundwater quality. Water of the study area shows mostly alkaline characteristics whereas some locations have pH less than 7. The pH of groundwater typically ranges from about 6.0 to 7.9, depending on type of adhering soil and rock. Reactions between groundwater and sandstone result in pH values between about 6.5 and 7.5, whereas groundwater flowing through dolomite strata has higher pH value. Water in contact with decaying organic matter can have pH value as low

Table 3. Correlation coefficients among various water quality parameters during pre-monsoon of 2015-16

	PH	EC	TDS	TH	Ca^{++}	Mg^{++}	Na^{+}	K^{+}	HCO_3^{-}	Cl^{-}	F^{-}	SO_4^{2-}	NO_3^{-}
PH	1	0.113	0.122	0.246	0.179	0.303	0.280	0.196	-0.001	0.190	-0.026	0.142	0.289
EC		1.000	0.992	0.634	0.716	0.275	0.213	0.172	0.401	-0.142	-0.049	-0.164	-0.037
TDS			1.000	0.646	0.734	0.282	0.226	0.172	0.412	-0.144	-0.050	-0.149	-0.045
TH				1.000	0.881	0.748	0.400	0.098	0.599	0.031	0.011	0.155	-0.053
Ca^{++}					1.000	0.397	0.327	0.148	0.501	-0.130	-0.080	0.056	0.001
Mg^{++}						1.000	0.423	0.043	0.548	0.188	0.091	0.196	-0.061
Na^{+}							1.000	0.363	0.478	0.117	0.116	0.069	-0.115
K^{+}								1.000	0.072	-0.198	-0.118	-0.261	0.103
HCO_3^{-}									1.000	0.050	0.100	0.152	-0.251
Cl^{-}										1.000	0.368	0.206	-0.136
F^{-}											1.000	0.065	-0.067
SO_4^{2-}												1.000	-0.080
NO_3^{-}													1

up to 4 and water reacted with shale have also lower pH value. The presence of free minerals also lowers the pH value.

The pre-monsoon samples of Ilukrishnanagar, Gurudijhatia, Khuntuni, Krushnashyampur and Gopalprasan depict higher sodium content, which exceeds the WHO limit. In the first year, the water samples of Champapur and Radhakishorpur in the post-monsoon period show a slightly saline character (as TDS<1000 is non-saline and TDS between 1000 and 3000 is slightly saline). Rest of the samples are non-saline and suitable for drinking purposes. In both the monitoring years TDS increases during post-monsoon period due to precipitation and environmental weathering. The TH value of water gradually increases in monsoon and post-monsoon periods, which indicates an increase in solubility of calcium and magnesium during the percolation of rainwater. The highest total hardness is found in the water sample of Gurudijhatia i.e., 513 mg/l in the post-monsoon period. Few locations show excess fluoride concentration, which may cause crippling of skeletal. Table 9 shows the groundwater of the study area is suitable for drinking and domestic use with few exceptions, as most of the parameters are within the permissible limits.

Water Quality Index analysis

Water Quality Indices for all the sampling locations are calculated for pre-monsoon, monsoon and post-monsoon of both the monitoring years, using the equations mentioned in the preceding section. The seasonal variation of WQI values and their suitability are classified into five categories: excellent, good, poor, very poor and unfit water for drinking purposes as shown in (Table 2). The study indicates that in pre-monsoon of both the years 74.6% to 77.3% of sample location comes under the "excellent" category, 22.6% to 40 % of the groundwater samples come under the "Good" category; 2.6% have been registered under the

Table 4. Correlation coefficients among various water quality parameters during monsoon of 2015-16

	PH	EC	TDS	TH	Ca^{++}	Mg^{++}	Na^{+}	K^{+}	HCO_3^{-}	Cl^{-}	F^{-}	SO_4^{2-}	NO_3^{-}
PH	1	-0.009	-0.012	0.163	0.041	0.080	0.037	-0.013	-0.111	0.055	-0.118	0.058	0.254
EC		1.000	0.997	0.654	0.738	0.306	0.223	0.151	0.257	-0.079	0.002	-0.102	-0.081
TDS			1.000	0.661	0.740	0.311	0.223	0.162	0.251	-0.096	0.007	-0.109	-0.072
TH				1.000	0.766	0.477	0.268	0.228	0.340	-0.184	-0.070	-0.049	0.037
Ca^{++}					1.000	0.401	0.305	0.113	0.307	-0.055	-0.061	0.008	-0.022
Mg^{++}						1.000	0.382	-0.082	0.196	0.137	0.296	0.104	-0.109
Na^{+}							1.000	0.366	0.137	0.045	0.329	0.084	-0.120
K^{+}								1.000	-0.053	-0.233	-0.062	-0.143	0.022
HCO_3^{-}									1.000	-0.137	0.032	0.033	-0.116
Cl^{-}										1.000	0.158	0.181	-0.048
F^{-}											1.000	0.187	-0.048
SO_4^{2-}												1.000	0.034
NO_3^{-}													1

Table 5. Correlation coefficients among various water quality parameters during post-monsoon of 2015-16

	PH	EC	TDS	TH	Ca^{++}	Mg^{++}	Na^{+}	K^{+}	HCO_3^{-}	Cl^{-}	F^{-}	SO_4^{2-}	NO_3^{-}
PH	1	-0.022	-0.048	0.157	0.180	0.085	-0.063	-0.191	0.160	-0.064	0.026	-0.187	0.053
EC		1.000	0.990	0.692	0.708	0.140	0.221	-0.053	0.414	-0.137	-0.036	-0.116	-0.059
TDS			1.000	0.656	0.661	0.142	0.223	-0.078	0.390	-0.144	-0.041	-0.130	-0.049
TH				1.000	0.933	0.344	0.074	0.034	0.699	-0.224	0.053	-0.173	-0.006
Ca^{++}					1.000	0.061	0.048	0.019	0.667	-0.214	-0.005	-0.214	-0.057
Mg^{++}						1.000	0.020	0.066	0.186	-0.125	0.215	-0.023	0.277
Na^{+}							1.000	0.261	0.272	0.233	-0.145	0.070	-0.106
K^{+}								1.000	0.212	-0.114	0.024	0.230	-0.029
HCO_3^{-}									1.000	-0.166	0.033	-0.018	-0.250
Cl^{-}										1.000	0.020	0.212	-0.134
F^{-}											1.000	0.030	0.091
SO_4^{2-}												1.000	-0.084
NO_3^{-}													1

"Unfit" category in pre monsoon of first year.

It demonstrates that the variations in water quality of the study area during the two consecutive monitoring years comparatively are not so significant and the average WQI of the study area comes under excellent to good category and can be used directly for domestic purpose. The increasing percentage of deterioration of quality is marked during monsoon, due to higher dissolution.

Analysis of Pearson's correlation coefficient (r) value

The results show the correlation between dependent

Table 6. Correlation coefficients among various water quality parameters during pre-monsoon of 2016-17

	PH	EC	TDS	TH	Ca^{++}	Mg^{++}	Na^{+}	K^{+}	HCO_3^{-}	Cl^{-}	F^{-}	SO_4^{2-}	NO_3^{-}
PH	1	0.497	0.489	-0.053	-0.196	0.112	-0.025	-0.218	0.060	-0.046	-0.086	-0.081	-0.197
EC		1.000	0.992	-0.036	-0.094	0.036	-0.063	0.023	0.078	0.064	-0.093	-0.052	-0.087
TDS			1.000	-0.011	-0.081	0.065	-0.045	0.037	0.111	0.025	-0.083	-0.065	-0.098
TH				1.000	0.837	0.828	0.421	-0.068	0.693	0.136	-0.060	0.303	0.209
Ca^{++}					1.000	0.387	0.361	-0.071	0.557	0.132	-0.020	0.343	0.375
Mg^{++}						1.000	0.340	-0.042	0.597	0.095	-0.081	0.159	-0.031
Na^{+}							1.000	0.197	0.529	0.341	0.044	0.169	0.243
K^{+}								1.000	0.007	0.100	0.172	-0.184	0.044
HCO_3^{-}									1.000	0.142	0.001	0.346	-0.097
Cl^{-}										1.000	0.047	0.246	0.050
F^{-}											1.000	0.174	0.085
SO_4^{2-}												1.000	-0.047
NO_3^{-}													1

Table 7. Correlation coefficients among various water quality parameters during monsoon of 2016-17

	PH	EC	TDS	TH	Ca^{++}	Mg^{++}	Na^{+}	K^{+}	HCO_3^{-}	Cl^{-}	F^{-}	SO_4^{2-}	NO_3^{-}
PH	1	-0.100	-0.100	0.045	0.126	-0.129	-0.033	0.133	-0.019	-0.065	-0.170	-0.019	0.231
EC		1.000	1.000	0.527	0.507	0.171	0.253	-0.001	0.527	-0.137	0.030	0.113	0.038
TDS			1.000	0.527	0.507	0.171	0.253	-0.001	0.527	-0.137	0.030	0.113	0.038
TH				1.000	0.867	0.490	0.194	0.054	0.797	-0.250	-0.078	0.251	0.200
Ca^{++}					1.000	-0.011	0.203	0.032	0.764	-0.185	-0.076	0.206	0.175
Mg^{++}						1.000	0.035	0.052	0.263	-0.178	-0.024	0.143	0.091
Na^{+}							1.000	0.282	0.416	0.075	0.244	0.206	0.274
K^{+}								1.000	0.132	-0.056	-0.103	0.056	0.173
HCO_3^{-}									1.000	-0.071	0.010	0.250	-0.152
Cl^{-}										1.000	0.273	0.118	-0.034
F^{-}											1.000	0.093	0.088
SO_4^{2-}												1.000	0.071
NO_3^{-}													1

Table 8. Correlation coefficients among various water quality parameters during post-monsoon of 2016-17

	PH	EC	TDS	TH	Ca^{++}	Mg^{++}	Na^{+}	K^{+}	HCO_3^{-}	Cl^{-}	F^{-}	SO_4^{2-}	NO_3^{-}
PH	1	-0.036	-0.036	0.120	0.154	-0.042	-0.031	-0.123	-0.020	0.071	-0.002	-0.268	0.154
EC		1.000	1.000	0.666	0.671	0.175	0.286	-0.007	0.652	-0.141	-0.092	-0.170	0.051
TDS			1.000	0.666	0.671	0.175	0.286	-0.007	0.652	-0.141	-0.092	-0.170	0.051
TH				1.000	0.920	0.464	0.024	0.032	0.778	-0.198	0.039	-0.096	0.217
Ca^{++}					1.000	0.079	0.004	0.018	0.768	-0.224	-0.030	-0.162	0.195
Mg^{++}						1.000	0.053	0.040	0.241	0.003	0.168	0.121	0.111
Na^{+}							1.000	0.152	0.278	0.200	-0.132	0.132	-0.056
K^{+}								1.000	0.196	-0.004	0.011	0.277	-0.041
HCO_3^{-}									1.000	-0.088	-0.031	0.026	-0.153
Cl^{-}										1.000	0.070	0.135	-0.119
F^{-}											1.000	0.061	0.060
SO_4^{2-}												1.000	-0.063
NO_3^{-}													1

and independent water quality parameters. It is evident that distribution of total dissolved solids, total hardness, calcium, magnesium and bicarbonate were significantly correlated (r > 0.5) with electrical conductivity in most of the study areas. pH values show positive correlations with TH, Ca^{+}, Mg^{2+}, Na^{+}, Cl^{-}, SO_4^{2-} and NO_3^{-}. Total hardness (TH) has been found to depict a positive correlation (r > 0.5) with Ca^{+}, Mg^{2+} and HCO_3^{-}. Calcium and bicarbonate demonstrate (r > 0.5) a positive correlation coefficient value in all the monitoring periods except the monsoon of 2015-16. Magnesium and bicarbonate also have positive correlation value (0.5 < r < 0.6). Fluoride is found to have positive correlation with sulphate and nitrate. A highly positive correlation is observed between EC and TDS (1.00 in the monsoon of 2016-17 and 0.997 in the monsoon of 2015-16), while a highly negative correlation coefficient is seen among potassium and sulphate (-0.261) during pre-monsoon of 2015-16.

Hydro-chemical facies Analysis

In the present study, water quality data is analyzed through statistical distribution diagrams such as Piper's trilinear diagram and Chadha's diagram by plotting the concentrations of major cations and anions to gain better insight into the hydrochemical processes operating in the groundwater flow system.

Piper's trilinear diagram

Piper trilinear diagram (Piper, 1944) is a widely used tool to understand the hydrochemical regime and facies classification of groundwater and surface water (Das *et al.*, 2010, 2015, 2016). Sample points with similar hydrochemistry tend to cluster together in the diagram.

The diagram reveals that the water of the study area belongs to the Ca–Mg-HCO_3 facies (Fig. 3). The prolific presence of calcium, magnesium and bicarbonate ions depict that the total hydro-geochemistry is dominated by alkaline earths and weak acids. The pre-monsoon has dispersed distribution, while the monsoon and post-monsoon have concentrated distribution. The seasonal variation indicates more complicated controlling factors. The higher concentration indicates high solubility of minerals during the monsoon and post-monsoon periods. The hydrochemical facies implies that the weathering of carbonate minerals is the primary controlling factor representing the seasonal variation.

Table 9. Descriptive statistics of water quality parameter of Athgarh basin and comparison of water quality with WHO (2004) and BIS 10500(2012) standards.

Parameter	Range Pre-monsoon **2015-2016**	Range Monsoon **2015-2016**	Range Post-monsoon **2015-2016**	Range Pre-monsoon **2016-2017**	Range monsoon **2016-2017**	Range Post monsoon **2016-2017**	WHO (2004)	IS-10500 (BIS, 2012) Highest desirable
pH	4.2-7.2	5.0-7.4	5.1-7.9	4.7-7.77	5.7-7.9	5.1-7.7	6.5-8.5	6.5
EC	28-1451	30-1524	56-2084	57.13-2108	49-1318	79-1742	400-2000	
TDS	18-928	19-975	14-1162	34.7-1196	32-843.52	50.56-1212.16	500-1000	500
Calcium	9-80	12-86	11-200	8.5-78	12-154	18-176	100-200	75
Magnesium	5-45	6-60	6-62	1.57-55.6	0.811-59.23	0.28-47.38	30-50	30
Sodium	1.7-75	9-45	11-43.1	6-71	8.5 – 46	8.7 – 51	20-175	
Potassium	4-29	4.1-22.5	3-24.5	5.2-27.5	5-29	6-27	10-12	
Bicarbonate	20.34-653	63.5-748	103-914	30.9-196	39-169	47-207		200
Sulphate	18-120	20-200	26-190	10.9-54.74	12.65-95.63	8.76-61.32	25-250	200
Chloride	30-250	25-360	18-290	12-87	9-77	16-84	25-600	250
Nitrate	0.76-47.8	1.05-45.35	1.25-45.21	2.46-37.8	1.05-33.25	1.25-35.45	45-100	45
Fluoride	.1024-1.7024	0.1002-1.986	.0524-2.21	0-2.31	0.09-2.08	0.08-1.89	0.15-2.32	1.0
Total Hardness	57-379	63-465	83-498	56.9-379.5	77-512	76-513		300

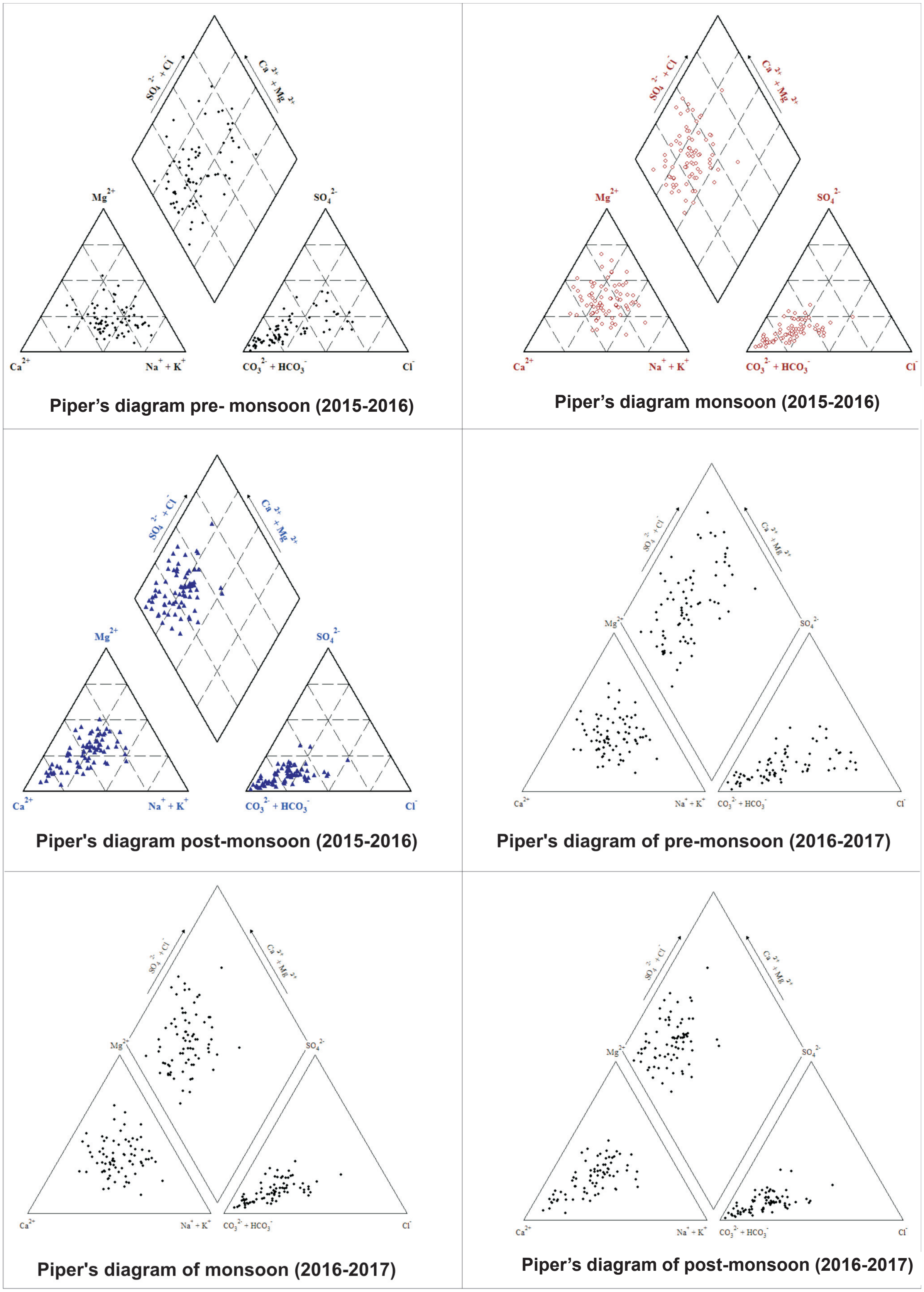

Fig. 3. Piper’s Trilinear diagram

Chadha's diagram

The hydrochemical diagram is proposed for the classification of natural waters and identification of hydrochemical processes. This diagram is constructed by plotting the difference in milliequivalent percentage between alkaline earths and alkali metals expressed as percentage reacting values, on the x-axis; and the difference in milliequivalent percentage between weak acidic anions and strong acidic anions expressed as percentage reacting values, on the y-axis. The milliequivalent percentage differences from x and y coordinates are extended further into the main study sub-fields of the diagram, which defines the overall character of water. This diagram suggested that the hydro-chemical facies belong to HCO_3^- dominant Ca^{2+}- Mg^{2+} type. The pre-monsoon samples show Cl^- dominant Ca^{2+}- Mg^{2+} type in some localities (Fig. 4).

CONCLUSION

Owing to the reliability and less vulnerability to pollution, groundwater samples were collected and analyzed. In the present work 75 groundwater samples were collected in three different seasons for two consecutive years and methodically assessed. With respect to the regular lithological variation throughout the basin the change in water quality is marked. On the basis of these analytical findings, the following conclusions are drawn.

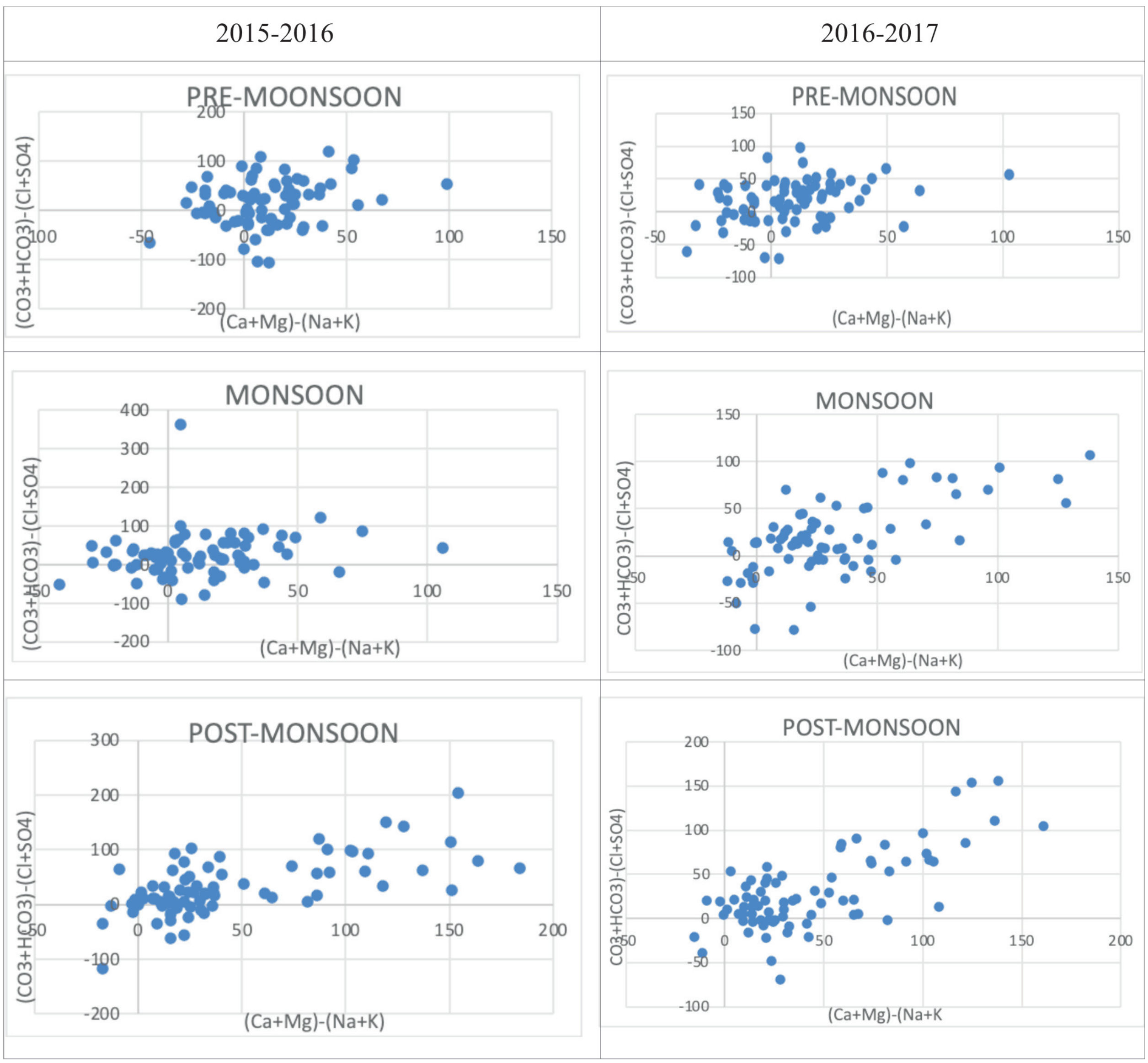

Fig. 4. Chadha's Diagram for hydrochemical determination

According to water quality index standards, the quality of water shows slight annual variation. The percentage of “Good” type water remains same during the pre-monsoon of the year 2015-2016 and 2016-2017. Only 2.6% of water comes under the “unfit” category for the year 2015-2016, which is not observed during 2016-2017. The average value of WQI is 42.75, 44.43, and 46.17 for pre-monsoon, monsoon and post-monsoon of 2015-2016 and 42.66, 48.8, 48.33 during pre-monsoon, monsoon and post-monsoon of 2016-2017, respectively. The annual variation in water quality index is not significant and major part of groundwater quality remains excellent and good for domestic purpose. The present study envisages the importance of graphical representations like Piper’s trilinear diagram and Chadha’s plot to determine hydrochemical facies and to understand the evolution of hydrochemical processes in the Athgarh basin. The analytical values obtained from the groundwater samples when plotted on Piper’s and Chadha’s plots revealed that the alkaline earth metals (Ca^{+}, Mg^{2+}) are significantly dominant over the alkalies (Na^{+}, K^{+}) and the weak acidic anion (HCO_3^{-}) dominant over the strong acidic anion (Cl^{-}, SO_4^{2-}). Further Piper trilinear diagram demonstrates most of the water samples of the study area are under Ca-Mg-HCO_3 type and few comes under Ca-Mg-Cl type. Interestingly, Chadha’s plot also demonstrated the dominance of permanent hardness (Ca-Mg-HCO_3 type). Thus, the evaluation of hydrochemical facies from both plots highlighted the significant contribution of alkaline earth metals (Ca^{+}, Mg^{2+}) and weak acidic anion (HCO_3^{-}), which might have been sourced from the dolomite and fireclay deposit in alternate layer of sandstone and shale.

Statistics of water quality parameter of Athgarh basin and its comparison with WHO (2004) and BIS 10500 (2012) standards demonstrate the variation of pH value. Water with high carbonate contents has high value of pH. Reactions between groundwater and sandstone result in pH values between 6.5 and 7.5, whereas groundwater flowing through dolomite strata has higher pH value. Groundwater from shale aquifer and presence of free minerals indicate lower pH value. Higher fluoride concentrations are reported from northwest and southeast of the study area. Numerous factors may influence the fluoride contamination in groundwater, including pH, rate of evaporation, temperature, composition of geologic formation. Higher concentration of fluoride in few locations during pre-monsoon indicates increased rate of evaporation. Higher potassium around agricultural land shows leaching of fertilizer from agricultural field. The variation in groundwater quality is due to varied geomorphic and geological set up which control the occurrence of groundwater reservoir. Statistical analysis demonstrates that the majority of water samples are suitable for domestic purposes. However, water samples around fireclay mine area, agricultural land and in high fluoride concentration patches require pretreatment before use.

The study reveals that all the parameters are more or less correlated. The linear correlation is very useful to get a fairly accurate idea of the quality of the ground water and to stop further vulnerability.

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