



Effects of Seasonal Variation on Major Ion Chemistry of Pahuj Reservoir, Jhansi, Uttar Pradesh, India

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Abstract:

Pahuj Reservoir, situated at north east part of district Jhansi, is the sole source of drinking water for the local people. The geochemical water quality of the reservoir was found under the influence of seasonal variation due to phosphate carbonate rock weathering and atmospheric precipitation. Hence, a detailed and systematic study was carried out to assess the concentration of major ions like HCO_3^- , Cl^- , SO_4^{2-} , PO_4^{3-} , NO_3^- , Ca^{2+} , Mg^{2+} , Na^+ and K^+ in reservoir for pre-monsoon, monsoon and post-monsoon in 2010. Through the statistical analysis it was observed that concentration of major ions in reservoir was found higher in pre-monsoon followed by post-monsoon and monsoon.

Keywords: Ion, Physicochemical, Reservoir, Seasonal Variation

1.0 Introduction:

Among all the renewable resource, water is unique (Kumar et. al., 2005) as the water quality directly affects the human welfare (Yadav et. al., 2012). Monitoring of water resource is of prime importance in developing countries like India as there water is commonly of economical and social significance (Tiwari and Singh, 2014). Indiscriminate disposal and discharge of industrial and domestic effluent caused various diseases due to the addition of high nutrient content, pathogens and hazardous chemicals in water (Yadav et. al., 2014).

A number of water bodies are found in India but most of them are anthropogenic typically tropics and very few are natural. Rivers, lakes and streams provide water supply for domestic, industrial and agricultural activities (Yusuf et. al., 2013). Thus water chemistry plays vital role to determine its use for industrial, domestic, agricultural purpose. The chemistry of surface water is regulated by evaporation, precipitation, rock weathering, and crystallization (Gibbs, 1970). Many factors like climate change, topography, soil characteristics, human activities on the ground, manner of water circulation through the rock etc. controls the quality

of water. Apart from these factors, the interaction between the surface water and the adjacent groundwater may also play vital role in determining the quality of the water.

Anthropogenic activities and changes in climate have changed the chemistry of water significantly several many years (Gopal, 2005). A number of lakes are found in north part of India are eutrophic due to yearly alteration in pattern of land-use (Chakrapani, 2005). Contaminants are reached in water catchment and hold by soil then transported to water body and uptake by living organisms and accumulate in the deposits/sediments (Njenga et. al., 2003). The water chemistry and type of pollutant changes the nature of the contaminants in the water column (Gopal, 2005).

Pahuj Reservoir is an important water resource in the Jhansi district as the water of Pahuj Reservoir is supplied in city for domestic purpose, fishing and agricultural activities etc. An experimental study on water chemistry of Pahuj Reservoir has not been done yet. The motive of the present study was to identify the effect of seasonal variation on major ion chemistry of Pahuj Reservoir. Major ion chemistry

explains the origin of solutes among anions and cations in water (Demile et. al., 2007; Tay, 2012; Wirmvem et. al., 2013).

2.0 Material and Methods:

2.1. Study Area:

Pahuj Reservoir lies at an approximate distance of 5 km from Jhansi city in north-west direction. The reservoir was established in 1909 and has a gross storage capacity of 18.25 MCM at full reservoir level. The length and height of the reservoir is 2040 m and 10.67 m respectively. The reservoir lies at 25°29'49.97"N latitude and 78°31'45.01"E longitude. The location of reservoir and sampling site is shown in Figure 1. The average annual rainfall is 850.1mm. The climate of the region is sub-humid and characterized by hot dry summer and cold winter. The reservoir is surrounded by steep hill slopes on three sides and it is artificially blocked on the other side.

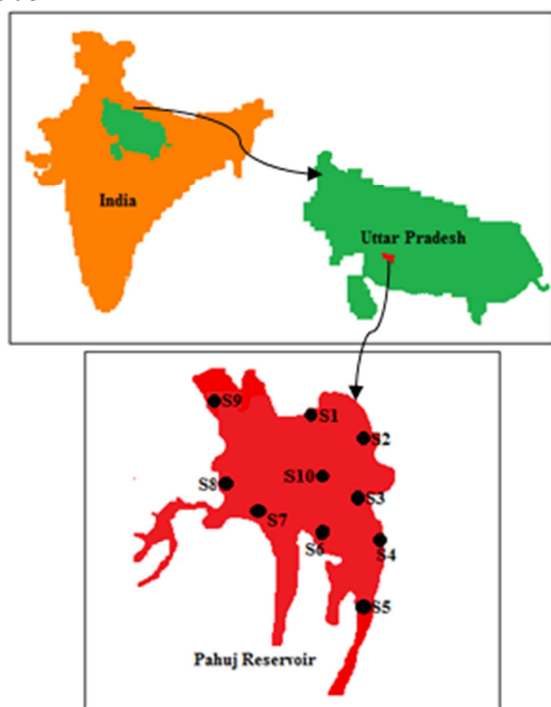


Figure 1: Map showing location of sampling sites

2.2. Collection of Samples:

Collection of water samples was done in pre-monsoon, monsoon and post-monsoon i.e. May, August and December 2010 respectively from 10 different locations. Triplicate of each sample were collected from each sampling site to remove the sampling error. During the collection of water samples, the water samples were filtered on site

every time using millipore filter of 0.45 and stored in pre-cleaned polypropylene bottles washed with nitric acid and rinsed with milli-Q water and labeled them properly. The polypropylene bottles were also washed with sample water at site prior to collect the sample. The samples collected for analysis of cation were acidified by 2 M HNO₃ to preserve them.

2.3. Chemical Analysis:

The pH, Electrical Conductivity, Optical Redox Potential, Total Dissolved Solids and Dissolved Oxygen were estimated on site by portable biocraft water analyzing kit viz model NPC 362D. The different methods were used to estimate the different parameter. The method of estimation of each parameter is given below in Table 1. Sample analysis was done by method given in APHA, 1994 using reagents of merck having high purity and milli-Q water of Milli-Q and Biocel model.

Table-1: Estimation method of analyzed parameters

Parameter	Estimation Method
Dissolved Oxygen	Winkler's method
HCO ₃ ⁻	Acid titration
Cl ⁻	Silver nitrate titration
SO ₄ ²⁻	Turbidimetric method
PO ₄ ³⁻	Ascorbic acid method
NO ₃ ⁻	UV spectrophotometric method
Dissolved Silica	Molybdsilicate method
Ca ²⁺	Titration method
Mg ²⁺	Titration method
Na ⁺	Flame photometric method
K ⁺	Flame photometric method

2.4. Statistical Analysis:

Pearson correlation was calculated to assess the relationship among various physicochemical parameters.

3.0 Result and Discussion:

3.1 Hydrochemistry of Surface Water:

The results shows that most of the physicochemical properties including major ion chemistry were found higher in the pre-monsoon followed by post-monsoon and monsoon. The analyzed results for all season are provided in Table 2. The water was found alkaline to some extent in all samples and found highest in post-monsoon samples (8.40±0.08) but

under the permissible limit (BIS, 1991). Seasonal fluctuation in pH regulates the presence of total dissolved solids in water and weathering pattern of rock. Electrical conductivity of a solution or substance is the assessment of capacity to carry the electrical current through the water (Gupta, 2013) which was higher in pre-monsoon samples (0.89 ± 0.06), followed by post-monsoon and monsoon samples respectively (0.68 ± 0.03 and 0.48 ± 0.05).

The estimation of the amount of oxygen dissolved in a liquid media, usually water is known as Dissolved oxygen (DO). DO is inversely proportional to temperature (Arya et. al., 2011), decomposition of organic matter and respiration rate of aquatic organisms (Sahu et. al., 2000; Saksena et. al., 2008). For fresh and healthy water its values should not be less than 6mg/L (BIS, 1991). The study shows that DO value for post-monsoon was 7.59 ± 0.20 , for monsoon was 6.37 ± 0.16 and for pre-monsoon it was noted 5.73 ± 0.31 , respectively. This indicates that water of Pahuj Reservoir is healthy as well as oxygenated.

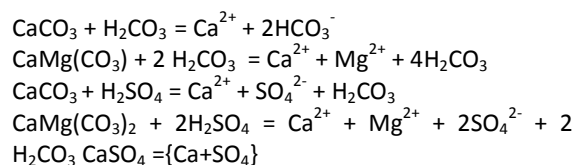
In this study, the high concentration of silicate (H_4SiO_2) was found in monsoon. It could be due to a reaction of carbonic acid in rainwater with almost minerals. It reacts at different rates with different mineral as per their stability. In present study, chloride (Cl^-) is observed as 66 ± 6.15 in pre-monsoon, 54.2 ± 4.77 in post-monsoon and 47.5 ± 7.83 in monsoon. The origination of Cl^- in water is rainfall coming from the Arabian Sea brought by monsoon winds. The high concentration of Cl^- in post-monsoon may be due to human activities like spreading of combination of salt and sand on road (Thomes, 1986; Stephenson, 1989; Minsk, 1989). The affinity of chloride is high towards sodium (Arya et. al., 2012).

The value of NO_3^- was found 9.04 ± 0.50 mg/L in pre-monsoon, 7.24 ± 0.34 mg/L in post-monsoon and 4.37 ± 0.42 mg/L in monsoon (Table 2). This point out that the water of Pahuj reservoir is clean as the concentration of nitrate is within the permissible limit i.e. 50 mg/L (EEC 1980; WHO 1984). Availability of nitrate in water represents that water is its final stage of mineralization (Nema et. al., 1984). The PO_4^{3-} in the Pahuj water is reported highest in pre-monsoon i.e. 17.44 ± 0.83 mg/L, followed by 15.66 ± 1.06 in post-monsoon and 12.32 ± 0.83 mg/L in monsoon (Table 2). This may be due to the leaching

of fertilizers applied on crops and decomposition of phytoplankton. The concentration of NO_3^- and PO_4^{3-} may be decrease due to the uptake by phytoplankton. Hence, it can be concluded that availability of NO_3^- and PO_4^{3-} in water is not due to any direct point source.

SO_4^{2-} concentration was found highest as 21.45 ± 0.61 mg/L (Table 2) in post-monsoon season, but in monsoon and pre-monsoon season, the concentration was found relatively low. This could be due to the high dissolution of secondary minerals in the reservoir sediments (Das and Kaur, 2001). Atmospheric deposition and oxidation of sulphur compounds occurs in the bottom sediments at the boundary layer between aerobic and anaerobic environment resulting origination of sulphate in the reservoir.

The abundance of dissolved major cations (Ca^{2+} , Mg^{2+} , Na^+ and K^+) and anions (SO_4^{2-} , HCO_3^- and Cl^-) in water can be modeled in terms of weathering of different minerals. Some scientists (Garrels, 1967) have shown some weathering reactions for minerals such as Dolomite [$CaMg(CO_3)_2$], Calcite ($CaCO_3$), and gypsum ($CaSO_4$) as follows:



A source of proton is required for the rapid weathering of carbonates. If the weathering agent is carbonic acid, the Ca: HCO_3^- ratio would be 1:2 for calcite weathering and 1:4 for dolomite weathering whereas if weathering agent is sulfuric acid, the Ca: SO_4 ratio in the water would be 1:1 for calcite weathering and 1:2 for dolomite weathering (Abu-Rukah and Ghrefat, 2004). In the present study, Ca: HCO_3^- ratio is about 1:4, indicating a possibility of dolomite weathering.

Calcium and magnesium was found major cations in the Pahuj Reservoir together contributes 78% of the total cations in pre-monsoon, 77% in monsoon and 76% in post-monsoon. The contribution of sodium and potassium is 22.6% among the major ion budget of the reservoir for all season. In Pahuj Reservoir water, HCO_3^- is the most abundant anion accounting for 39-45% of total anions followed by chloride (30-40%) and phosphate (9-12%). The concentration of

HCO_3^- was found 81.5 ± 0.84 mg/L in post-monsoon, 70.15 ± 6.43 mg/L in pre-monsoon and 61.86 ± 2.63 mg/L in monsoon season respectively (Table 2). This might be due to weathering of carbonate rocks at surface sediment.

The $(\text{Ca}^{2+} + \text{Mg}^{2+})/\text{Tz}^+$ is 0.21 in pre-monsoon, 0.11 in monsoon and 0.13 in summer. This ratio shows the enrichment of Ca^{2+} and Mg^{2+} in the reservoir and indicates the carbonate weathering. The average ratio $(\text{Na}^+ + \text{K}^+)/\text{Tz}^+$ for pre-monsoon, monsoon and post-monsoon are 0.22, 0.23 and 0.24 respectively. This ratio concludes that the carbonate weathering is dominant in comparison to aluminosilicate weathering. The molar $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio in pre-monsoon, monsoon and post-monsoon is less than <1.0 indicates a low saturation index and carbonate precipitation. The availability of major cations and anions in monsoon may be due to the atmospheric precipitation but in pre-monsoon and post-monsoon it may be due to the chemical weathering and atmospheric precipitation both (Anshumali and Ramanathan, 2007). Composition of natural water is controlled by chemical weathering (Garrels, 1967; Bricker and Garrels, 1967; Hem, 1985; White, 2002). Natural water accumulates the cations in water as it is the common weathering agent.

3.2 Correlation Matrix:

The correlation matrix among physico-chemical parameters for pre-monsoon, monsoon and post-monsoon is given in Table 3, 4 and 5 respectively. A strong relationship has been observed between NO_3^- and Ca^{2+} ; HCO_3^- and Mg^{2+} ; DO and K^+ ; H_4SiO_2 and NO_3^- in pre-monsoon whereas in monsoon pH and EC; TDS and HCO_3^- , HCO_3^- and Mg^{2+} ; Cl^- and NO_3^- was strongly correlated. H_4SiO_2 and Na^+ ; NO_3^- and PO_4^{2-} ; SO_4^{2-} and Ca^{2+} was strongly correlated in post-monsoon.

3.3 Trilinear Explanation/ Piper Diagram:

A trilinear diagram, also known as a Piper diagram (Piper, 1944) gives an easiest way to classify and compare the water type based on the ionic composition of various water samples (Hem, 1985) using Aqua Chem 5.1 software. Cation and anion concentrations for each season samples are plotted in two triangles as percentages of their respective totals and then projected into a quadrilateral polygon that explains the water type or hydrochemical faces. Fig 3a, 3b and 3c represent Piper diagrams for pre-monsoon, monsoon and post-monsoon respectively. It also shows that Ca^{2+} and

Mg^{2+} are the most prevalent cations and HCO_3^- is the dominant anion in Pahuj Reservoir. So, this water could be classified as calcium- bicarbonate type. From the figure it is also clear that most of the samples fall into the normal earth alkaline water group with prevailing bicarbonate and sulphate (Fig 3b). This type of water originates through natural processes by the dissolution of carbon dioxide (CO_2) from the atmosphere and from the soil horizon which causes the dissolution of the carbonate minerals, dolomite (Ca/MgCO_3), calcite (CaCO_3) of the aquifer (Suk and Lee, 1999).

Table 2: Average results of physico-chemical properties of Pahuj Reservoir

Parameter	Pre Monsoon			Monsoon			Post Monsoon		
	Ave± Std	Min	Max	Ave± Std	Min	Max	Ave± Std	Min	Max
pH	7.53±0.09	7.40	7.70	6.73±0.13	6.50	6.90	8.4±0.08	8.30	8.50
EC	0.89±0.06	0.79	0.97	0.48±0.05	0.41	0.55	0.68±0.03	0.63	0.73
TDS	630±38.37	570.00	675.00	320.80±25.82	280.00	360.00	430.50±34.96	380.00	490.00
DO	5.73±0.31	5.30	6.22	6.37±0.16	6.10	6.70	7.59±0.20	7.30	7.90
H ₄ SiO ₂	84±7.75	70.00	95.00	109.5±11.06	90.00	120.00	60.5±4.15	55.00	65.00
Cl ⁻	66±6.15	50.00	70.00	47.5±7.83	40.00	60.00	54.2±4.77	50.00	65.00
NO ₃ ⁻	9.04±0.50	8.20	9.50	4.37±0.42	4.00	5.30	7.24±0.34	6.70	7.80
PO ₄ ²⁻	17.44±0.83	15.80	18.90	12.32±0.83	11.00	14.20	15.66±1.06	14.50	17.50
SO ₄ ²⁻	15.84±0.80	14.50	16.70	17.94±0.51	17.00	18.90	21.45±0.61	20.00	22.00
HCO ₃ ⁻	70.15±6.43	60.00	80.00	61.86±2.63	58.50	65.80	81.5±0.84	80.00	82.50
Na ⁺	9.45±0.60	8.00	10.00	4.09±0.59	3.00	5.20	6.08±0.65	5.00	7.00
K ⁺	0.98±0.17	0.80	1.20	0.40±0.04	0.35	0.45	0.80±0.08	0.60	0.90
Ca ²⁺	20.3±1.57	18.00	22.00	10.55±0.99	8.50	12.00	15.71±1.02	14.00	17.60
Mg ²⁺	16.9±1.52	15.00	19.00	4.83±0.50	4.00	5.60	6.29±0.62	5.00	7.20
T _z ⁺	47.63±2.52	42.90	51.40	19.87±1.64	16.75	21.80	28.88±0.73	27.60	30.30
T _z ⁻	178.47±7.18	163.70	187.00	143.99±8.76	134.15	155.80	180.05±4.81	175.30	192.50
Ca ²⁺ /SO ₄ ²⁻	1.28±0.10	1.08	1.38	0.59±0.05	0.49	0.67	0.73±0.04	0.67	0.80
Ca ²⁺ /HCO ₃ ⁻	0.29±0.04	0.24	0.37	0.17±0.01	0.14	0.20	0.19±0.01	0.17	0.22
Mg ²⁺ /Ca ²⁺	0.83±0.10	0.68	1.00	0.46±0.05	0.38	0.53	0.40±0.05	0.29	0.47
Ca ²⁺ Mg ²⁺ /Na ⁺ +K ⁺	1.07±0.17	0.88	1.31	0.51±0.05	0.45	0.61	0.87±0.08	0.67	0.96
Ca ²⁺ Mg ²⁺ /T _z ⁺	0.21±0.02	0.19	0.24	0.11±0.01	0.08	0.13	0.12±0.01	0.11	0.13
Na ⁺ +K ⁺ /T _z ⁺	0.22±0.01	0.20	0.25	0.23±0.02	0.20	0.27	0.24±0.02	0.20	0.28
H ₄ SiO ₂ /Na ⁺ +K ⁺	8.05±1.05	6.73	10.11	24.38±4.85	18.75	35.29	8.79±0.65	7.79	10.31

• Unit for all parameter is mg/l except EC; EC in µS/cm

Table 3: Correlation analysis among all parameters for pre-monsoon

Parameter	pH	EC	TDS	DO	H ₄ SiO ₂	Cl ⁻	NO ₃ ⁻	PO ₄ ²⁻	SO ₄ ²⁻	HCO ₃ ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺
pH	1													
EC	0.399	1												
TDS	-0.168	-0.560	1											
DO	-0.112	-0.209	-0.016	1										
H ₄ SiO ₂	0.348	-0.171	0.019	-0.004	1									
Cl ⁻	-0.002	-0.059	-0.204	-0.566	0.266	1								
NO ₃ ⁻	-0.216	-0.582	0.365	0.051	0.672	0.069	1							
PO ₄ ²⁻	-0.087	-0.018	-0.387	-0.251	0.180	0.141	0.325	1						
SO ₄ ²⁻	0.100	0.561	-0.692	-0.135	0.322	0.113	-0.063	0.111	1					
HCO ₃ ⁻	-0.445	-0.294	0.359	0.310	-0.432	-0.329	-0.326	-0.535	-0.230	1				
Na ⁺	0.127	-0.192	-0.048	-0.171	-0.371	-0.116	-0.123	0.474	-0.438	-0.265	1			
K ⁺	-0.097	-0.238	0.017	0.683	0.238	-0.372	0.551	0.213	-0.159	-0.335	0.044	1		
Ca ²⁺	0.082	0.354	-0.730	-0.219	-0.110	0.137	-0.301	0.758	0.318	-0.347	0.492	-0.143	1	
Mg ²⁺	-0.438	0.105	0.000	0.286	-0.762	-0.613	-0.491	-0.146	-0.097	0.716	0.055	-0.138	0.060	1

Table 4: Correlation analysis among all parameters for monsoon

Parameter	pH	EC	TDS	DO	H ₄ SiO ₂	Cl ⁻	NO ₃ ⁻	PO ₄ ²⁻	SO ₄ ²⁻	HCO ₃ ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺
pH	1													
EC	0.67	1												
TDS	-0.32	-0.38	1											
DO	0.36	0.52	0.00	1										
H ₄ SiO ₂	0.48	0.11	-0.02	0.07	1									
Cl ⁻	-0.17	-0.03	-0.29	-0.49	0.07	1								
NO ₃ ⁻	0.46	0.49	-0.78	-0.17	0.16	0.57	1							
PO ₄ ²⁻	-0.05	-0.07	0.42	0.03	-0.19	0.32	-0.18	1						
SO ₄ ²⁻	-0.34	-0.42	0.54	-0.14	-0.25	-0.56	-0.72	-0.14	1					
HCO ₃ ⁻	-0.09	-0.54	0.63	-0.23	0.21	0.06	-0.26	0.46	0.17	1				
Na ⁺	0.24	0.13	-0.22	-0.32	-0.21	0.31	0.56	-0.16	-0.12	0.07	1			
K ⁺	-0.01	0.54	-0.34	-0.03	-0.02	0.31	0.23	-0.19	-0.10	-0.77	-0.03	1		
Ca ²⁺	-0.09	-0.43	0.36	-0.24	-0.25	-0.47	-0.22	-0.20	0.52	0.46	0.44	-0.66	1	
Mg ²⁺	0.02	-0.27	0.28	-0.28	0.25	0.26	0.09	-0.11	0.15	0.59	0.56	-0.26	0.35	1

Table 5: Correlation analysis among all parameters for post-monsoon

Parameter	pH	EC	TDS	DO	H ₄ SiO ₂	Cl ⁻	NO ₃ ⁻	PO ₄ ²⁻	SO ₄ ²⁻	HCO ₃ ⁻	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺
pH	1.00													
EC	0.33	1.00												
TDS	-0.24	-0.17	1.00											
DO	0.38	0.16	0.21	1.00										
H ₄ SiO ₂	0.16	-0.35	-0.07	0.07	1.00									
Cl ⁻	-0.41	-0.29	0.48	-0.35	0.45	1.00								
NO ₃ ⁻	0.38	0.38	-0.08	0.21	-0.12	-0.04	1.00							
PO ₄ ²⁻	0.52	0.52	0.26	0.39	0.08	0.10	0.59	1.00						
SO ₄ ²⁻	-0.32	-0.32	-0.33	0.20	-0.29	-0.67	-0.25	-0.56	1.00					
HCO ₃ ⁻	0.34	0.49	0.32	0.33	0.00	0.18	0.14	0.36	-0.64	1.00				
Na ⁺	0.34	0.34	0.34	0.47	0.67	0.42	0.05	0.46	-0.49	0.42	1.00			
K ⁺	0.41	0.41	-0.11	-0.41	-0.02	-0.01	0.44	0.01	-0.31	0.12	-0.10	1.00		
Ca ²⁺	0.05	0.05	-0.42	-0.03	-0.14	-0.61	-0.02	-0.13	0.59	-0.48	-0.65	-0.08	1.00	
Mg ²⁺	-0.27	-0.27	-0.14	-0.15	-0.44	0.01	0.33	0.22	0.00	-0.33	-0.13	-0.08	-0.27	1.00

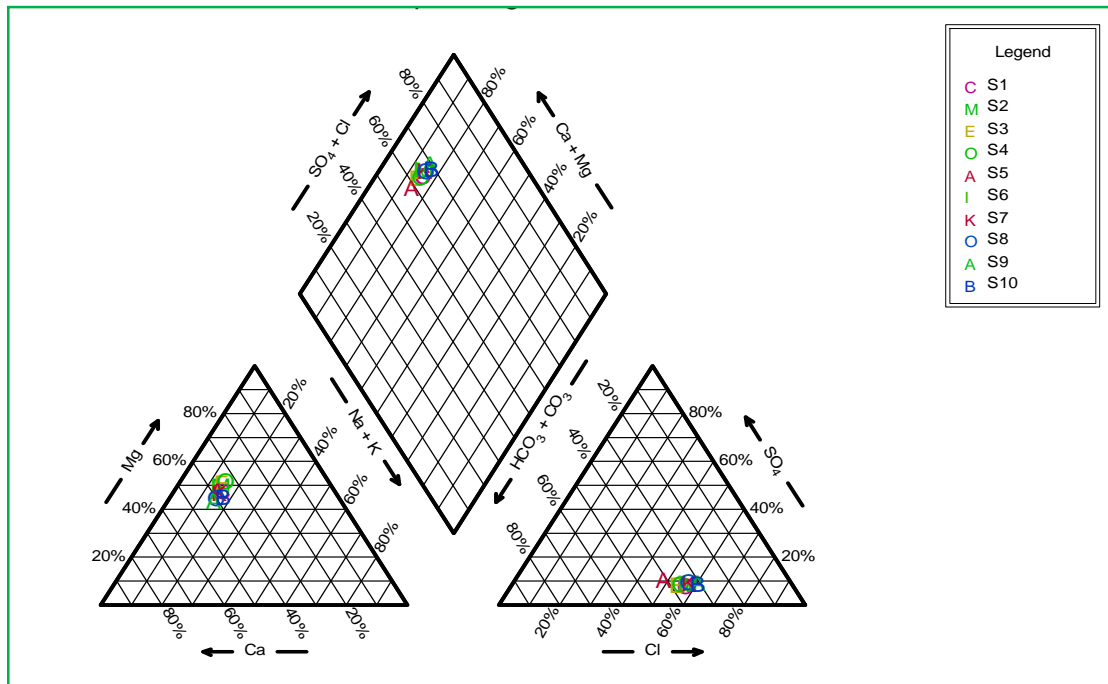


Figure 3a: Piper Diagram for Pre-Monsoon

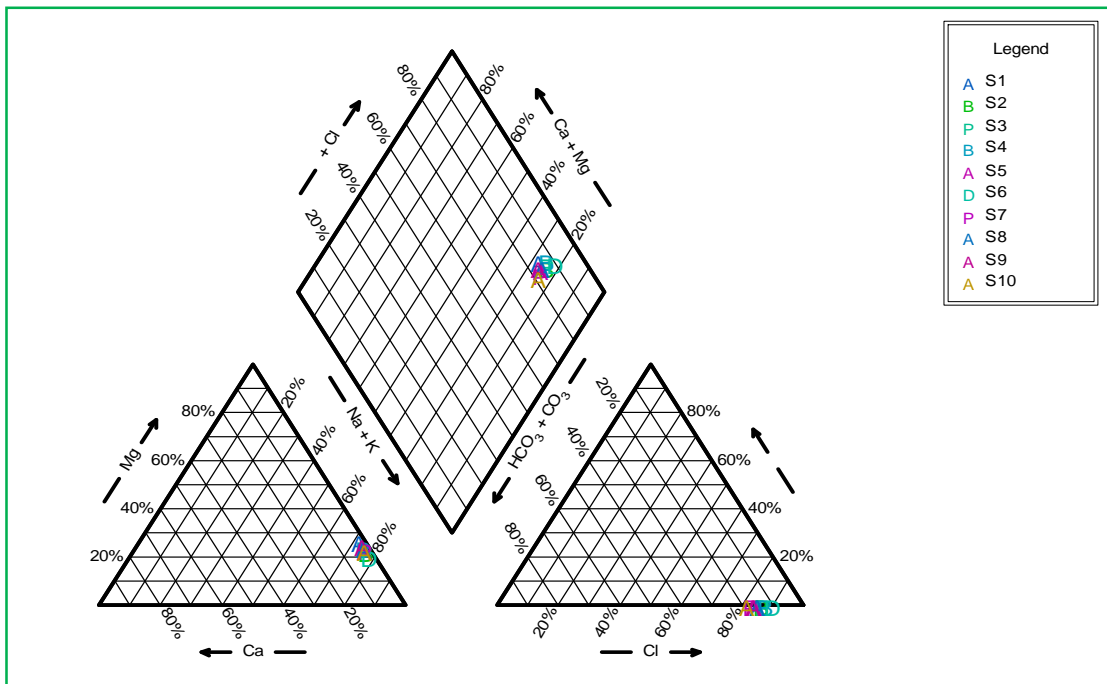


Figure 3b: Piper Diagram for Monsoon

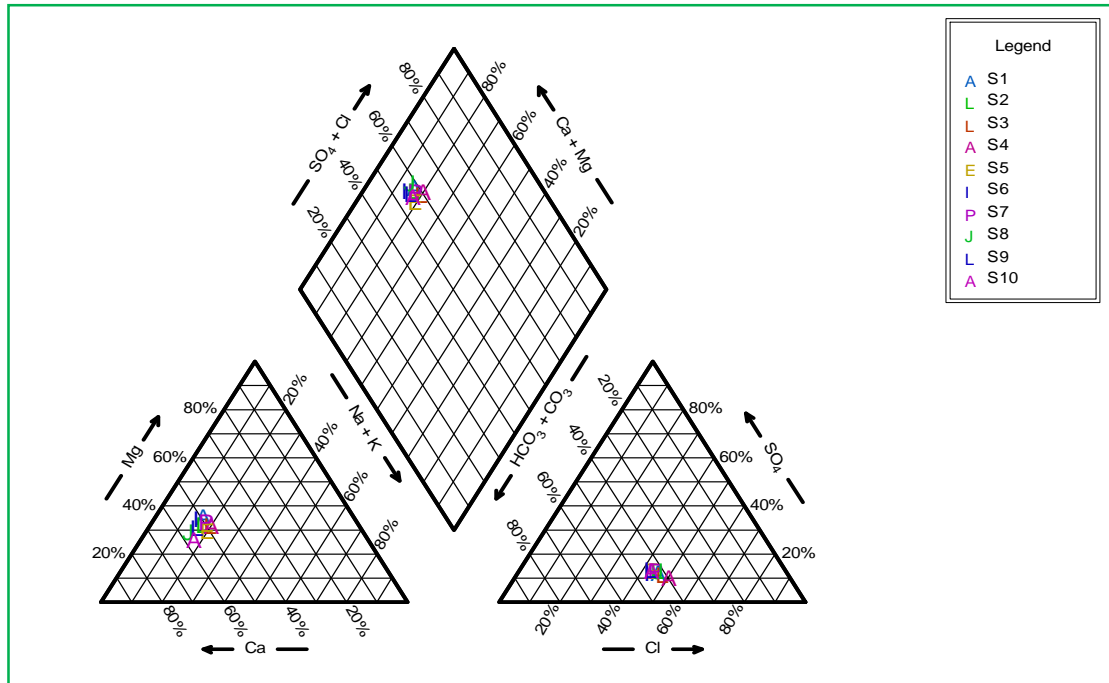


Figure 3c: Piper Diagram for Post-Monsoon

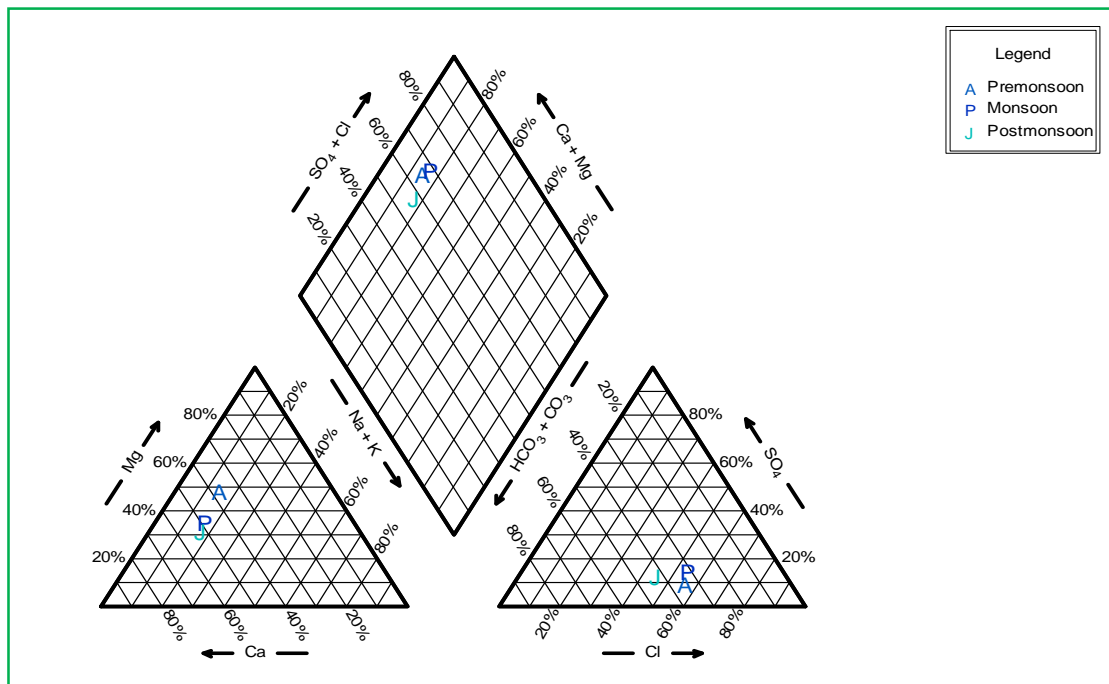


Figure 3d: Piper Diagram for Pre-Monsoon, Monsoon and Post-Monsoon

4.0 Conclusion:

This study elucidates the seasonal behavior of major ions that directly or indirectly influence the water chemistry. The physical parameters like pH, EC, TDS and DO were in good quantity and shows Pahuj Reservoir is a fresh water body. The water is slightly alkaline due to weathering of bed rocks. Major ions shows a trend like pre-monsoon > post-monsoon > monsoon. Calcium is dominant cation followed by magnesium. Sodium is dominant over potassium, due to weathering of the silicate minerals of igneous and metamorphic rocks. Most of the sodium comes through weathering of sodium plagioclase but chloride source is due to atmospheric input. Bicarbonate is the major anion followed by sulphate.

Correlation matrix suggests that carbonate weathering is dominated in Pahuj Reservoir followed by silicate weathering. High $\text{Ca}^{2+}/\text{SO}_4^{2-}$ ratio (>1) would results no reaction between the carbonate mineral and H_2SiO_4 for weathering. Weathering of silicate minerals and carbonate minerals would be the results of $\text{SiO}_2/(\text{Na}^++\text{K}^+)$ and $(\text{Ca}^{2+} + \text{Mg}^{2+}/\text{HCO}_3^-)$ ratio in water respectively. Dominant cations are represented by $\text{Ca}^{2+}+\text{Mg}^{2+}/\text{T}_z^+$ and $\text{Na}^++\text{K}^+/\text{T}_z^+$ ratio and provide abutment to carbonate minerals in the sediment and catchment area. Seasonal fluctuation in the major cation ratio is the indication of multiple mineral sources. Ion chemistry of water is also influenced by seasonal variation in the environmental factors like rainfall, temperature and wind speed. Physical and chemical change in water may also occur due to the time to time release of water from the reservoir. The $\text{Mg}^{2+}/\text{Ca}^{2+}$ ratio shows that the impact of carbonate weathering to water chemistry is very high.

Seasonal fluctuations in the major ions control the reservoir activities and reflect the indivisible nature of the biotic and abiotic components running in the reservoir ecosystem.

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