

Geochemical and statistical evaluation of groundwater in the Thamirabarani river basin, south India

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Abstract

In the present study, an attempt has been made to develop the dictate metrics using a multi-proxy approach, i.e., spatial-temporal analysis, statistical evaluation, and hydrogeochemical analysis for 45 water samples located in the Thamirabarani river basin in Tamil Nadu, India. In order to evaluate the aptness of developed metrics for agriculture and domestic needs, eleven years dataset was analyzed and compared with national and international standards. Monitoring and analysis results revealed that the concentration of calcium and chloride ion was on the higher side in all the selected locations. These higher values may be attributed to the regional point sources such as untreated water disposal and off-peak sources such as agriculture practices. The principal component analysis resulted in 84.2% of the total variance in the post-monsoon season dataset. The major analyzed cations and anions were observed in the following order: $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ and $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{NO}_3^-$, respectively. Overall, this study revealed that the studied area's groundwater quality was significantly affected by the high salinity in the region, probably due to anthropogenic activities and unprotected river sites.

1. Introduction

Water is one of the most vital components of the environment and is considered a major lifeline of humans and society. Further, being an inevitable part of the ecosystem and flora-fauna, water plays an essential role in the survival of soil, water, and air environment associated micro-organisms (Kisi and Ay, 2014). Such concerns undoubtedly suggest that water quality and quantity are crucial in ensuring the earth's environment's sustainability living and non-living entities. The condition of water quality in developing countries is also not untouched by regional activities (both natural and anthropogenic), ultimately resulting in deteriorated water resources (Zhou et al., 2013). Having this background understanding, groundwater quality analysis becomes of utmost importance to ensure its utility for urban and rural activities (Anandakumar et al., 2009). Such water scarcities issues were also raised in 1992 in Rio de Janeiro during the U.N. Conference on Environment and Development. Later in 2017, the water wastage issues were discussed by U.N. member nations, emphasizing drinking water scarcity worldwide (Sujatha, 2017). Moreover, the groundwater levels are also declining (Sinha et al., 2019; Shekhar et al., 2020), and the increasing rate of deterioration of the water quality (Sajitha and Vijayamma, 2016).

Nowadays, water qualitative and quantitative concerns for water resources are growing worldwide, especially in Asian countries like China, India, Bangladesh. Among these countries, water contamination in Indian states is a severe concern, depending on different pollutants (microbial, organic and inorganic). In addition to this, India also faces frequent issues of floods and droughts, which also increases groundwater pollution (Thillai Arasu et al., 2007). The groundwater quality is also affected by anthropogenic activities (i.e., waste disposal and agricultural waste) and natural processes (mineral dissolution and geochemical reactions). This ultimately led to less per capita water availability in India (Joarder et al., 2008; Kumar, 2013).

On the other side, water supply demands for drinking, household activities, agriculture and industrial purposes are significantly based on groundwater sources (Joarder et al., 2008). In this context, the quality indices can be derived using anions and cations elements for any given basin (Saedi et al., 2010). A detailed assessment of various usage patterns of groundwater quantitative and qualitative determination of water resources (physical, chemical and biological) plays an essential role (Selvakumar et al., 2017). Among all characteristic's types, chemical characteristics of groundwater are affected by anthropogenic activities and are well documented for developing countries like India, China, Bangladesh. However, the attention paid to these concerns is minimal, and water resources management needs urgent action, especially in semi-arid and arid regions (Alaa et al., 2016).

Bearing these considerations in mind, the present study aimed to analyze groundwater by using multi-proxy approaches (spatial-temporal analysis, statistical evaluation, and hydro-geochemical analysis) for the impact prediction of groundwater pollutants around the Thamirabarani river basin.

2. Study Area And Methodology

A mixture of waste chemicals, leachate, and groundwater are usually in solution form, but other insoluble forms are possible. One such groundwater quality analysis for Tamirabarani River has been analyzed and interpreted using AquaChem, AqQA, Time Trend and ArcGIS environment. The parameters like Ca, Mg, Na, K, HCO_3^- , CO_3 , SO_4 , Cl, NO_3^- , pH, EC, and TDS from 45 sampling locations were analyzed for pre- and post-monsoon seasons during 2016 and 2017. In the present study, we have compiled historical data from 1995 to 2007 from Tamilnadu Public Work Department Data Centre. Here, in the present study, we prepared time-series, Durov, Piper, Box and Whisker, Scatter, Stiff, Schoeller, Wilcox, Cross, Ion balance diagram, Radial and Pie diagram based on geochemical parameters.

2.1. Study Area

The focus area is the Thamirabarani river basin, located in Tamil Nadu in India (Fig. 1). The geographical extent of the study area is from $8^{\circ}8' \text{N}$ to $9^{\circ}23' \text{N}$ latitude and from $77^{\circ}09' \text{E}$ to $77^{\circ}54' \text{E}$ longitude and covers an area of about 5665 km^2 . The climate condition of the study area is considered a semi-arid region. The annual rainfall of the study area is about 680 mm. The Thamirabarani River is perennial in the study area, which is a major source for irrigation practices.

2.2. Sampling and analysis

The water samples were collected from 45 locations in the study area during pre- and post-monsoon seasons from 2016 to 2017 (Fig. 1). Also, we compiled historical water quality data from 1995 to 2006 from Tamilnadu Public Work Department Data Centre. The water samples were collected from bore wells and dug wells located within the study area and analyzed for water quality parameters (pH, EC, TDS, Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , HCO_3^- , CO_3 , SO_4^{2-} , and NO_3^-). The standards methods (APHA, 1999) were used for the sampling and analysis of collected data. Determination of hydro-geochemical facies provides sufficient information on the groundwater system's chemical water quality (Kumar, 2013). The hydro-geo-chemical analysis has carried out using AqQA software. Trend

analysis was carried out for the identified sample locations to know the temporal pattern of groundwater quality (Jones et al., 2013; Jones et al., 2015) in the study area. Principal Component Analysis (PCA) was used to identify the actual status of physio-chemical parameters in collected samples. This method helps in extracting different factors to identify the predominant variable using factor analysis. In PCA, to extract factors, the varimax rotation has been used. PCA technique is used to reduce the data, and it will suggest how many varieties are essential to explain the observed variance in the data. Statistically, the correlation between the statistical variable analyses performed on the physico-chemical parameters.

3. Results And Discussion

The descriptive statistical analysis of groundwater quality data collected during pre- and post-monsoon seasons is shown in Table 1. It observed that out of 45 sample points, a higher mean concentration of conductivity has recorded. Some wells exceed for calcium and magnesium hardness, respectively. The permissible limit for Cl^- , SO_4^{2-} , HCO_3^- , and NO_3^- have violated 100% of the samples. The chemical composition of collected data sets have been analyzed statistically, and a comparison has been made with international standards (Table 1). The observed results indicated the alkaline nature of groundwater quality with pH ranging between 7.2 and 8.4.

The electrical conductivity (EC) values of water samples; the observed results vary from 1324 $\mu S/cm$ to 2374 $\mu S/cm$, indicating higher salinity and dissolved ionic concentration. Reported values (5000 mg/l) of TDS during sampling have been higher than the international standards (WHO; 1000 mg/l) for drinking the maximum allowable TDS values. The higher values of TDS have been observed due to the percolation of channel water containing solids, agricultural wastes, and industrial seepages through the country rocks (Offor et al., 2015). The reported higher concentration values 236 mg/l, 429 mg/l, 1018 mg/l, 106 mg/l for Ca^{2+} , Mg^{2+} , Na^+ , and K^+ ions, respectively. According to cation concentration, the sequence has been arranged; $Ca^{2+} > Mg^{2+} > Na^+ > K^+$. This study's outcomes highlighted that most of the samples (approximately more than 70%) are beyond the permissible limits, like 200, 150, 200, and 12 mg/l, for Ca^{2+} , Mg^{2+} , Na^+ , K^+ , respectively.

Table 1
Summary of statistics of water samples collected during the present study

Parameters		pH	Cond	TDS	Na	K	Mg	Ca	Cl	SO4	HCO3	CO3	NO3	
Descriptive statistics				(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	(mg/l)	
Post monsoon	Jan 2016	Max	8.65	8318	5000	1018	106	429	236	2752	396	358	65	27
		Min	7.65	320	188	16	1	18	15	34	8	110	1	1
		Mean	8.13	1324.7	779.1	132.9	19.5	59.6	58.7	285.7	73.3	209.3	21.6	5.8
		Std. dev	0.22	1256.1	745.4	151.4	19.4	61.5	45.7	426.7	67.4	55.5	11.9	4.8
	Jan 2017	Max	8.40	6925	3606	920	235	240	316	1679	464	1354	199	115
		Min	7.20	210	110	12	1	7	20	18	2	67	3	1
		Mean	7.80	2239.9	1327.5	236.3	39	83.4	95.6	465	123.7	278.1	29.2	32.5
		Std. dev	0.24	1387.8	793.3	204.5	45.2	46.1	52.4	343.6	102.6	188.3	33.3	23.1
Pre monsoon	Jul 2016	Max	9.20	14930	8660	1535	194	349	1126	4937	527	629	213	102
		Min	7.60	504	274	14	2	20	28	55	16	94	1	2
		Mean	8.40	2349.2	1381.7	226.2	34.2	95.3	114.4	558.8	133.9	224.9	33.5	30
		Std. dev	0.25	2374.9	1395.5	254.6	43.8	81.3	166.7	814.1	123.4	93.5	33.6	23.5
	Jul 2017	Max	8.50	9953	5580	1163	91	418	460	3151	266	653	46	30
		Min	7.70	465	254	30	2	16	30	44	6	128	2	1
		Mean	8.10	1527	871.7	145.7	17.6	61.1	82	326.8	74.8	240.5	22.9	7.2
		Std. dev	0.16	1567.1	875.6	174.9	18.6	66.6	77.8	501	69.2	97.7	10.2	6.6
Standards	WHO (2011)	7.0–8.5	-	600–1000	200	-	30–100	75–200	200–300	200–400	500	-	45–100	
	BIS (2012)	6.5–8.5	-	500–2000	200	-	100	75–200	250–1000	200–400	400	-	45–400	
	ICMAR	6.5–8.4	250	500	-	-	-	-	70	-	-	-	45	

3.1. Correlation Analysis

The correlation coefficient is generally used in evaluating the relationship between two variables. Pearson's correlation analysis applied to the post-monsoon (July 2016 and 2017) presented in Tables 2 and 3 show the correlation coefficient between the major ions in the

study area. Suppose the values of the correlation coefficient 'r' between the variable are large. In that case, it implies the two variables are highly correlated; in such case, it gets split to linear relation $Y = Ax + B$ (Gajendran and Thamarai, 2008).

$$r = \frac{\left(\bar{X} - \bar{X} \right) \left(\bar{Y} - \bar{Y} \right)}{\sqrt{\left(\left(\bar{X} - \bar{X} \right)^2 \left(\bar{Y} - \bar{Y} \right)^2 \right)}}$$

The value of 'r' in positive correlation lies between 0 to 0.99 (Gajendran et al., 2013). A significant positive correlation among various indicators was evident. Conductivity has a significant correlation with TDS, Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , and SO_4^{2-} with $r = 0.67$ to 0.98 in post-monsoon. Correlation in post-monsoon has a significant correlation between TDS, Na^+ , Mg^{2+} , Cl^- , HCO_3^- and SO_4^{2-} with $r = 0.66$ to 0.97 . In pre- and post-monsoon seasons, TDS, Na^+ , Mg^{2+} , Ca^{2+} , Cl^- , and SO_4^{2-} with $r = 0.79$ to 0.99 and $r = 0.61$ to 0.99 , respectively.

A significant and high positive correlation was obtained for Ca^{2+} , Mg^{2+} , Na^+ , K^+ , and Cl^- and SO_4^{2-} with TDS. The strong correlation of Mg^{2+} ion with Cl^- ($r = 0.966$). The variation of these relationships indicates the entanglement of the groundwater's hydro-chemical components, where natural water always contains dissolved and suspended substances of minerals. The source of Mg^{2+} and Na^+ in the groundwater was the ion exchange of minerals between rocks and water. NO_3^- ion positively high correlated with Cl^- ($r = 0.67$), which indicates the contamination from septic systems, fertilizers, municipal wastewaters, and sometimes the cultivation of grasslands.

Table 2
Pearson's correlation of groundwater quality for post-monsoon.

January 2016													January 2017				
	pH	Cond	TDS	Na	K	Mg	Ca	Cl	SO4	HCO3	CO3	NO3	pH	Cond	TDS	N	
pH	1												pH	1			
Cond	-.048	1											Cond	0.124	1		
TDS	-.037	0.998	1										TDS	0.174	0.977	1	
Na	.006	0.979	0.985	1									Na	0.217	0.944	0.932	1
K	.239	0.733	0.746	0.746	1								K	0.261	0.438	0.518	0.
Mg	.022	0.966	0.969	0.956	0.700	1							Mg	0.116	0.740	0.786	0.
Ca	-.323	0.670	0.653	0.549	0.380	0.512	1						Ca	-0.14	0.569	0.583	0.
Cl	-.023	0.991	0.992	0.977	0.719	0.966	0.654	1					Cl	0.167	0.901	0.953	0.
SO4	-.089	0.871	0.877	0.859	0.705	0.859	0.497	0.822	1				SO4	0.145	0.878	0.860	0.
HCO3	-.167	0.174	0.165	0.183	0.178	0.150	0.066	0.089	0.210	1			HCO3	0.034	0.665	0.530	0.
CO3	.464	0.549	0.562	0.586	0.647	0.590	0.081	0.524	0.559	0.204	1		CO3	-0.12	0.127	0.126	0.
NO3	-.204	0.279	0.275	0.212	0.182	0.214	0.351	0.202	0.488	-0.022	0.173	1	NO3	0.073	0.407	0.501	0.

Bold values indicates good correlation ($r > 0.60$)

Table 3
Pearson's correlation of groundwater quality for pre monsoon.

July 2016													July 2017					
	pH	Cond	TDS	Na	K	Mg	Ca	Cl	SO4	HCO3	CO3	NO3	pH	Cond	TDS	Na	K	
pH	1												pH	1				
Cond	-0.25	1											Cond	0.008	1			
TDS	-0.26	0.99	1										TDS	0.017	0.999	1		
Na	-0.13	0.95	0.95	1									Na	0.132	0.938	0.944	1	
K	-0.08	0.33	0.35	0.36	1								K	0.195	0.617	0.622	0.653	1
Mg	-0.39	0.85	0.86	0.71	0.43	1							Mg	-0.03	0.984	0.980	0.889	0.57
Ca	-0.26	0.91	0.90	0.81	0.03	0.70	1						Ca	-0.17	0.819	0.812	0.590	0.30
Cl	-0.25	0.98	0.97	0.92	0.28	0.85	0.91	1					Cl	0.01	0.991	0.988	0.936	0.58
SO4	-0.27	0.79	0.80	0.71	0.41	0.83	0.65	0.74	1				SO4	-0.05	0.729	0.745	0.601	0.41
HCO3	-0.05	0.22	0.24	0.30	0.25	0.20	0.06	0.12	0.36	1			HCO3	0.100	0.364	0.372	0.410	0.32
CO3	-0.18	0.56	0.56	0.46	0.25	0.68	0.46	0.62	0.55	0.273	1		CO3	0.427	0.259	0.272	0.351	0.44
NO3	-0.40	0.31	0.34	0.16	0.39	0.60	0.19	0.28	0.48	0.222	0.47	1	NO3	-0.091	0.169	0.184	0.093	0.33

Bold values indicates good correlation ($r > 0.60$)

3.2. Principal Component Analysis (PCA)

In this study, a statistical tool (PCA) has been used for collected 45 water samples to assess the relationship between hydro-chemical composition and available factor/physio chemical parameters to identify the actual status of water quality. The PCA results (i.e., Eigen values, percentage of the total variance, etc.) is summarized in Table 4.

Table 4
Factor analysis scores (Varimax rotation) of various physicochemical parameters in the study area:

Factor analysis	Parameter														
	January 2016			January 2017				July 2016			July 2017				
	1	2	3	1	2	3	4	1	2	3	1	2	3		
pH	0.094	-0.892	-0.213	0.040	-0.08	0.890	-0.07	-0.15	-0.81	0.176	-0.19	0.731	-0.133		
Cond	0.977	0.157	0.023	0.904	0.383	0.123	0.089	0.967	0.160	0.181	0.979	0.168	0.091		
TDS	0.982	0.138	0.018	0.822	0.499	0.223	0.116	0.958	0.169	0.205	0.975	0.182	0.107		
Na	0.970	0.058	0.060	0.882	0.221	0.222	0.144	0.929	-0.04	0.250	0.887	0.347	-0.011		
K	0.823	-0.224	0.061	0.355	0.256	0.563	-0.05	0.154	0.198	0.711	0.513	0.519	0.296		
Mg	0.958	0.040	0.029	0.529	0.539	0.218	0.424	0.752	0.500	0.305	0.972	0.104	0.112		
Ca	0.584	0.582	-0.111	0.383	0.749	-0.24	-0.28	0.948	0.120	-0.17	0.861	-0.16	0.197		
Cl	0.964	0.125	-0.035	0.682	0.568	0.266	0.172	0.971	0.173	0.096	0.979	0.118	0.015		
SO4	0.897	0.168	0.032	0.865	0.272	0.129	0.019	0.710	0.317	0.421	0.705	0.058	0.552		
HCO3	0.162	0.071	0.942	0.875	-0.27	-0.08	-0.07	0.106	-0.09	0.771	0.321	0.556	-0.058		
CO3	0.683	-0.529	0.098	0.081	-0.01	-0.13	0.946	0.503	0.368	0.362	0.096	0.842	0.254		
NO3	0.308	0.419	-0.306	0.051	0.868	0.109	0.078	0.115	0.778	0.427	0.066	0.024	0.972		
Eigen values	7.126	1.739	1.060	4.813	2.594	1.454	1.247	5.953	1.899	1.874	6.229	2.059	1.495		
% of variance	59.38	14.48	8.834	40.10	21.61	12.11	10.39	49.60	15.82	15.61	51.91	17.15	12.45		
Cumulative %	59.385	73.873	82.707	40.10	61.7	73.8	84.2	49.6	65.4	81.4	51.9	69.6	81.5		

The loading of chemical parameters is > 0.75, 0.75 to 0.50, and 0.50 to 0.30 for strong, moderate, and weak, respectively. PCA results in 84.2% of the total Loading [MathJax]/jax/output/CommonHTML/jax.js n season. The more than 0.65 values of chemical parameters loading are considered significant. Several studies

used this technique to interpret the groundwater quality (Hotelling, 1933; Helsel and Hirsch, 2002; McBride, 2005; Visser et al., 2009; Belkhiri et al., 2010; Kim and Chung, 2011; Bhat et al., 2014). For Factor I, 59% (pre-monsoon) and 40% (post-monsoon) of the total variance showing strong positive loadings on EC, TDS, Mg^{2+} , Na^+ , K^+ , CO_3 as well as Cl^- and SO_4^{2-} , which indicating significant interference of anthropogenic activities in mineral water reaction. On the other hand, 14%, 8.83% of the total variance has been observed for Factor II and Factor III, respectively. The results from the PCA suggested that the set of natural soluble salts explains most of the variations.

3.3. Time-series Analysis

Two kinds of approaches have been developed to predict water quality parameters. One is time-series prediction, while the other predicts the water quality parameters without considering the time head (Guoyin and Zhang, 2015). Time-series analysis is a forecasting method used to predict future value based on the previously observed value (Deng and Wang, 2017; Conrads et al., 2007; Sun and Koch, 1996; Ragavan and Fernandez, 2010; Faruk, 2010; Akkaraboyina and Raju, 2012; Mirsanjari and Mohammadyari, 2018). The water samples collected from 45 sampling stations with various water quality parameters like pH, EC, TDS, Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , HCO_3^- , CO_3 , SO_4^{2-} , and NO_3^- . TDS in post and pre-monsoon (Jul 2016 and 2017) of station number TM-240, TM-244, TM-54, and TM-295 have loaded with a high concentration of TDS (Fig. 2).

3.4. Hydro-geochemical Analysis

To understand the hydro-geo-chemical evolution of groundwater in the study area, we are determined by plotting various diagrams such as Ion balance diagram, Piper Trilinear, Durov plot, scatter plot, Wilcox plot, Cross plot, Pie diagram, Radial plot, Stiff diagram and Schoeller diagram. The overall checking of the cation-anion balance in the sample is to validate the water test results. If the analysis is accurate, then the sum of milliequivalents of cations and anions should be nearly equal (Srinivasamoorthy et al., 2011; Xiao et al., 2016). More than 5% of the cation-anion balance error might imply that the analysis is not accurate. The accuracy is calculated by the ion balance errors, generally within ± 5 (Narany et al., 2014). However, if the laboratory did not test for one of the essential cations or anions, then a correct balance cannot be calculated (Hoaghia et al., 2015; Dalai et al., 2002). The relative ion concentration is represented graphically in Fig. 3.

According to the ion balance diagram, all 45 water samples Cl^- and Na-K type. In post-monsoon season SO_4^{2-} is the lowest concentration, and in the pre-monsoon season, both SO_4^{2-} and HCO_3^- are the lowest ionic concentration. Piper diagram is a graphical representation of the chemistry of water samples (Fig. 4). It is suitable for comparing the ionic composition of a set of water samples. In the piper diagram, the cations and anions have shown by separate ternary plots. These plotted points in triangular fields are projected in the central diamond field, which helps determine the overall character of the water (Sajil Kumar, 2013). The total cations in meq/l and the total anions in meq/l are set equal to 100% of the water sample.

Datasets are displayed as a diamond grid in Fig. 4 to show the total ion relationships—three data points in each triangle representing the individual sample (Babu et al., 2015). The assessment of geochemical properties was estimated by concentration (meq/l) levels of anions (HCO_3^- , SO_4^{2-} and Cl^-) and cations (Ca^{2+} , Mg^{2+} , Na^+ and K^+) in collected groundwater samples. Several researchers have conducted similar types (Yang et al., 2016; Mapoma et al., 2016; Krishna et al., 2015; Suma et al., 2015). In Fig. 6, 60%, 15%, 15%, and 10% of samples representing the quality of water like mixed types Na-Mg-Ca-Cl- HCO_3 , Na-Mg-Ca-Cl type, Na-Mg-Cl- HCO_3 and Na-Mg-Cl, respectively, whereas in anion triangle are showing chloride type, dominant type and bicarbonate type with 70%, 20% and 10%, respectively, which indicated that water is approximately 70% salted in nature.

To determine water-based major cations – anions in collected samples Durov diagram are presented in Fig. 5 (Gomo and Vermeulen, 2014), where two separate triangle plots are presenting the cations and anions values (Azaza et al., 2011; Nagaraju et al., 2016). According to previous studies (Azaza et al., 2011; Fiky, 2010; Chang and Wang, 2010), data plotted in the base of the triangle and lies perpendicular to the third axis in each triangle are provided information about vertex elements concentration which lost in the square grid. In Durov diagram (Fig. 5), the TDS and pH values are graphically represented by cationic and anionic concentration.

The result shows that in the post-monsoon season, TM 240 and TM 259 water samples have a higher value for TDS and in the pre-monsoon season, water samples of TM 59 and TM 295 have a higher concentration on TDS. Since TDS concentration in groundwater exceeds 1000 mg/l in both post-monsoon and pre-monsoon indicates that the groundwater is generally saline or brackish. Brackish water has a TDS concentration in the range between 1000 to 10000 mg/l. The determination of variability of water irrigation purpose has been done by Wilcox plot, where It classifies according to sodium hazard (SAR) and salinity hazard (conductivity) (Srinivasamoorthy et al., 2014). The interpretation, through EC vs. SAR values, of water quality suitable for the irrigation purpose. SAR has been estimated from the incremental ionic concentration of Na^+ , Ca^{2+} , and Mg^{2+} according to the following relationship (Velasco et al., 2014).

$$SAR = Na / \sqrt{\left(\frac{Ca + Mg}{2}\right)}$$

Where the quantities of Ca^{2+} , Mg^{2+} , and Na^+ are expressed in milliequivalents per liter.

The concentration levels of minerals determine the suitability of water for irrigation to show its effects on soil and plants (Rammohan and Jeevanandam 2009). Earlier studies indicated a higher concentration of sodium in the soil, displace the available Mg^{2+} , and Ca^{2+} ions. In this regard, soil having low permeability and showing poor internal drainage (Helsel and Hirsch, 2002; Sadashivaiah et al., 2015). Figure 6 shows that water suitability for irrigation purposes has been presented, where values indicated that 70% of collected samples fall in permissible limits (Selvakumar et al., 2017; Das et al., 2015; Hua et al., 2015).

The relationship between sodium adsorption and electrical conductivity is demonstrated using the US salinity diagram (Wilcox diagram). The analytical data outcomes indicated that 70% of samples are falling on the C3S1 type category and indicating high salinity and low sodium content. The results highlighted that it could be useful for irrigation in all soil types to provide a low risk of exchangeable sodium. On the other side, 20% of samples are identified in C2S1, which indicates samples containing low alkalinity content and medium salinity. Such types of samples are very much suitable for plants having good salt tolerance.

In Fig. 7, a scatter plot indicating the influence of one variable on other variables (Umar et al., 2009). The scatter plot constructed for all sample data measured during 2016 and 2017 is presented (Figs. 7 & 8). Here two quality variables are sampled at the same time. In post-monsoon season Fig. 6, the 93030 samples have a higher correlation between Ca^{2+} and Mg^{2+} . As a result, the Ca^{2+} increase concerning magnesium indicates that the hardness of the water samples is more. In Figs. 6 and 7, 93105 samples correlated with potassium and sodium. The sodium-rich groundwater occurs rock salt-bearing strata.

In Fig. 8, it can be seen that a good correlation has been found between Cl^- and Na^+ through 93030 samples. As a result, the Cl^- increases concerning Na^+ indicates that high salinity in a water sample.

In the cross plot, dissolved solids and calcium correlated during study periods. In post-monsoon, Fig. 9 station TM-49 (Jan 2016) and TM-259 (Jan 2017) positively correlated between calcium and dissolved solids. In pre-monsoon, station TM-54 (Jul 2016) and TM-57 (Jul 2017) positively correlated between calcium and dissolved solids. The ratio of the concentration of major ions of individual samples has been plotted by using Pie charts. All parameters have been customizable using different colors and patterns (Qingchun Yang et al., 2016). The pie diagram (Fig. 10) shows that chloride and magnesium are the dominant anions and cation, respectively.

The total chloride (mg/l) has been reported 34.2% and 41.6% in post- and pre-monsoon time. According to higher concentration, the order of major cations in collected samples are $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$, while $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-}$ has been reported for anions in study area. Semi – logarithmic diagrams indicate major ion analysis (meq/l) with different hydro-chemical water types (Uzoije et al., 2014). The actual sample concentrations are displayed and compared are the main advantage of this graphical representation, like trilinear diagrams (Narany et al., 2014). In Fig. 11, the Schoeller diagram is presenting a plot of all samples in the open database. A total of 12 different parameters are demonstrated along with the x-axis. The symbols represent the sample points in a customized manner into shape and color. All the highlighted lines are indicated specific samples selected in the database (Zaidi et al., 2016; Fianko et al., 2010). Cations (Na^+ , K^+ , and Mg^{2+}) and anions (Cl^- , SO_4^{2-} , and HCO_3^-) have been plotted on the right and left sides, respectively. The higher concentration of Cl^- ion indicated the salt content in the selected study area.

In Fig. 12, radial diagrams have been plotted for a single sample as the graphically comparing the measured parameter concentration for several individual samples. Kumar et al. (2006) reported that radial diagrams are handy for identifying different water facies' geographic locations with the same composition. An average of 12 chemical parameters has been presented using two clusters in the stiff diagram. In this regard, Na^+ and Cl^- are observed as dominant cation and anion, respectively (Uzoije et al., 2014).

4. Conclusion

A comprehensive assessment has been done to develop groundwater quality fluctuation factors in selected study sites “semi-arid region of Thamirabarani river” during monsoon (Pre & Post) season by analyzing and interpreting 45 samples. The physicochemical result determines the groundwater is generally alkaline. The higher concentration of selected ions has been observed in the following order, $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ < \text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{NO}_3^-$. On the other hand, Ca–Mg– HCO_3^- , Mg–Ca–Cl, Na–Cl, and infused waters have been identified in the basin area, which is not representing anion and cation dominates. Due to increased concentration chloride in a water sample indicates that it is unsuitable or causes major problems for drinking purpose, this is mainly caused due to the inappropriate discharge of domestic sewage, excessive application of agricultural fertilizers and also due to the abundant growth of population which may lead to groundwater deterioration in the surrounding environment.

Declarations

Conflict of Interest

There is no conflict of interest.

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Figures

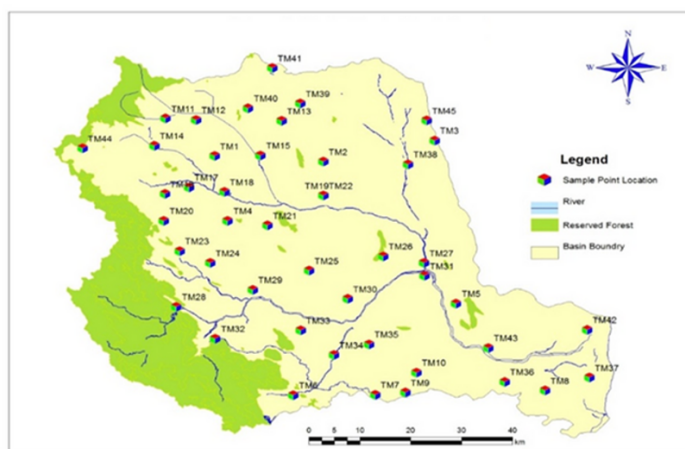
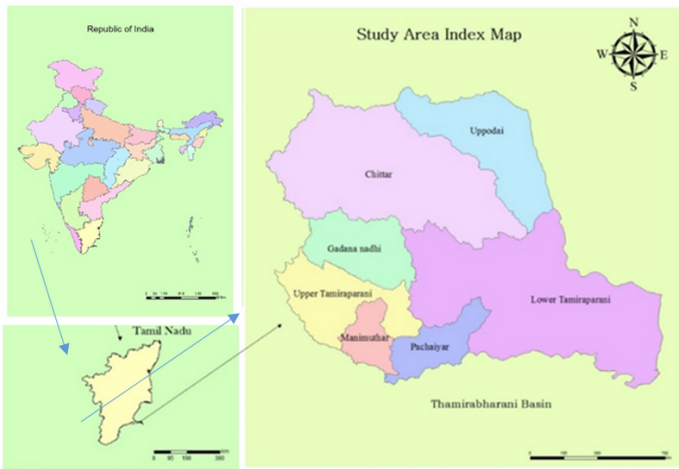


Figure 1
 Thamirabarani river basin in Tamil Nadu, India. Note: The designations employed and the presentation of the material on this map do not imply the expression of any opinion whatsoever on the part of Research Square concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. This map has been provided by the authors.

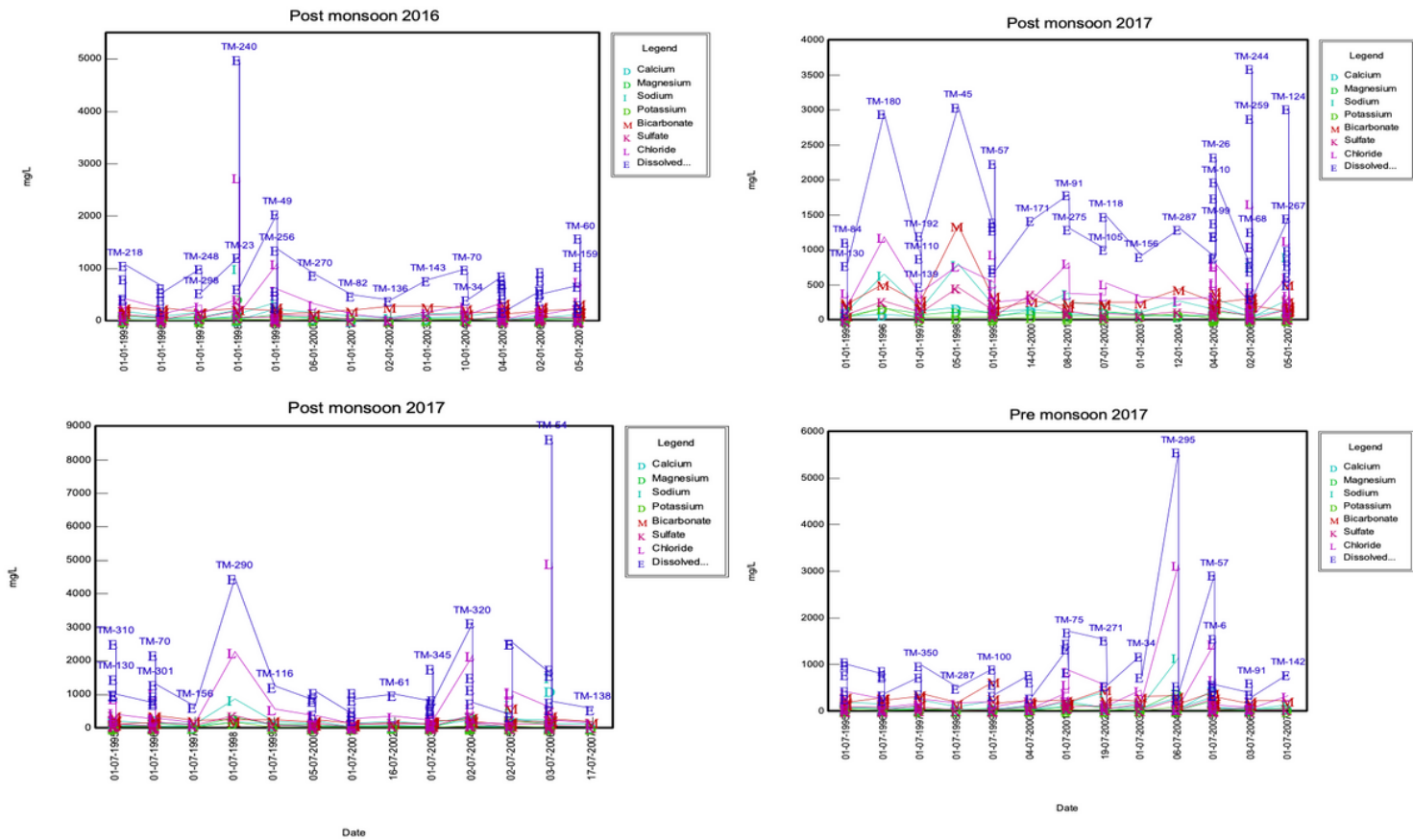


Figure 2

Time series analysis for post and pre-monsoon.

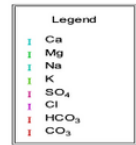
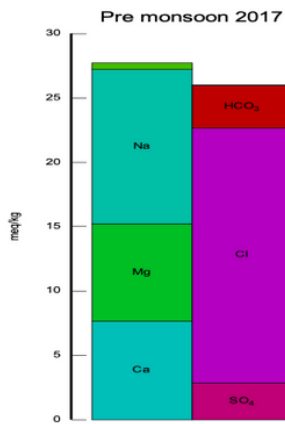
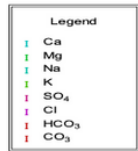
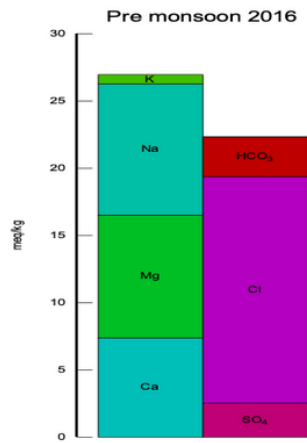
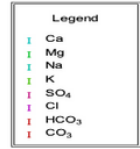
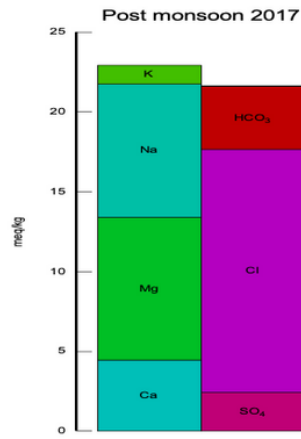
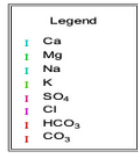
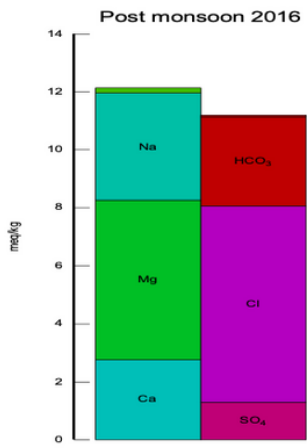


Figure 3

Ion balance diagram for post and pre-monsoon.

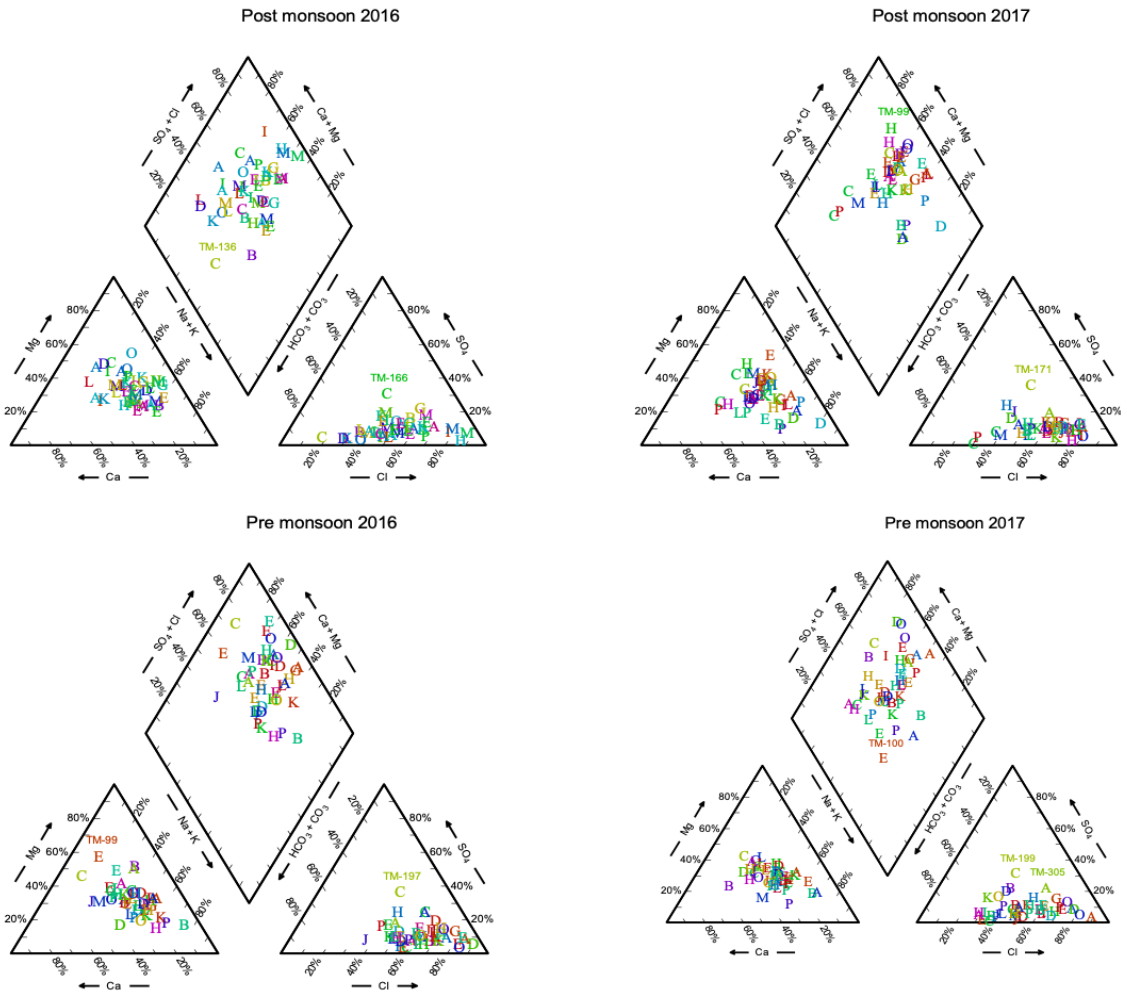


Figure 4

Piper trilinear diagram for post and pre-monsoon

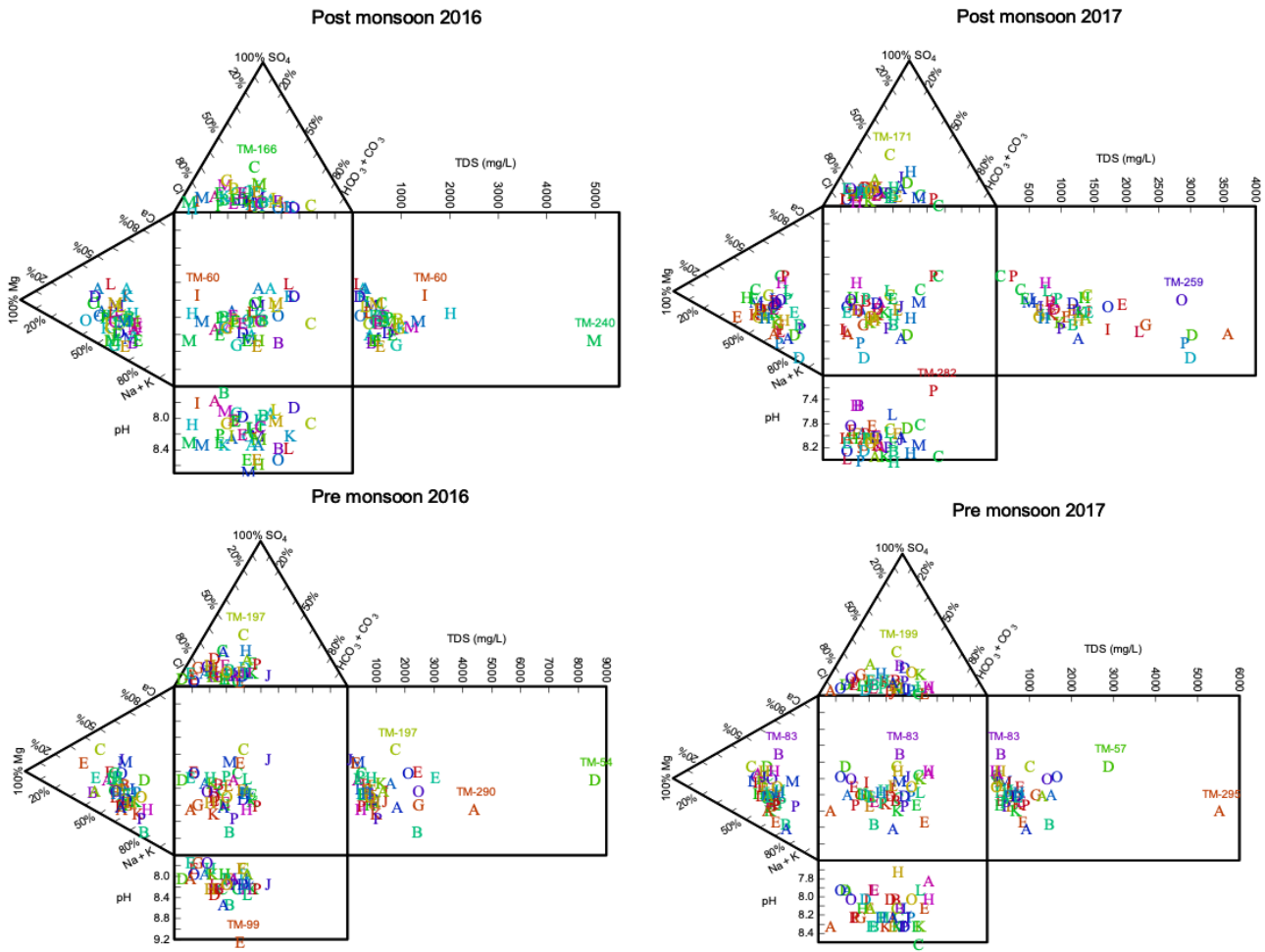


Figure 5

Durov plot for post- and pre-monsoon

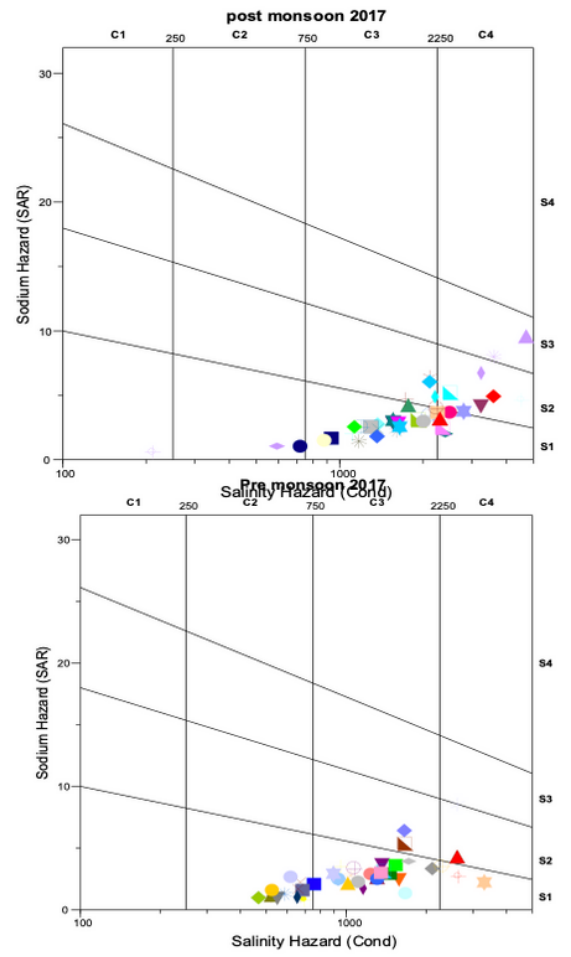
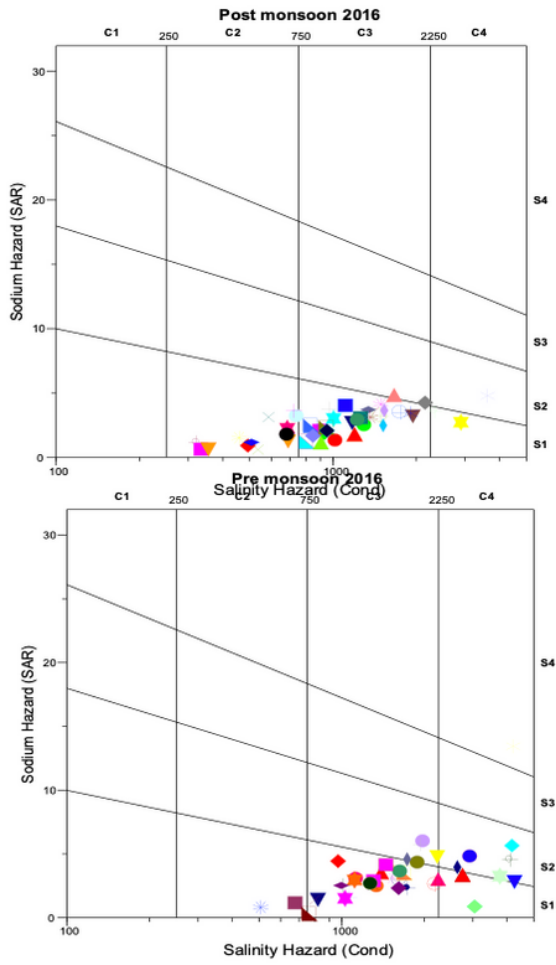


Figure 6

Wilcox diagram for post and pre-monsoon.

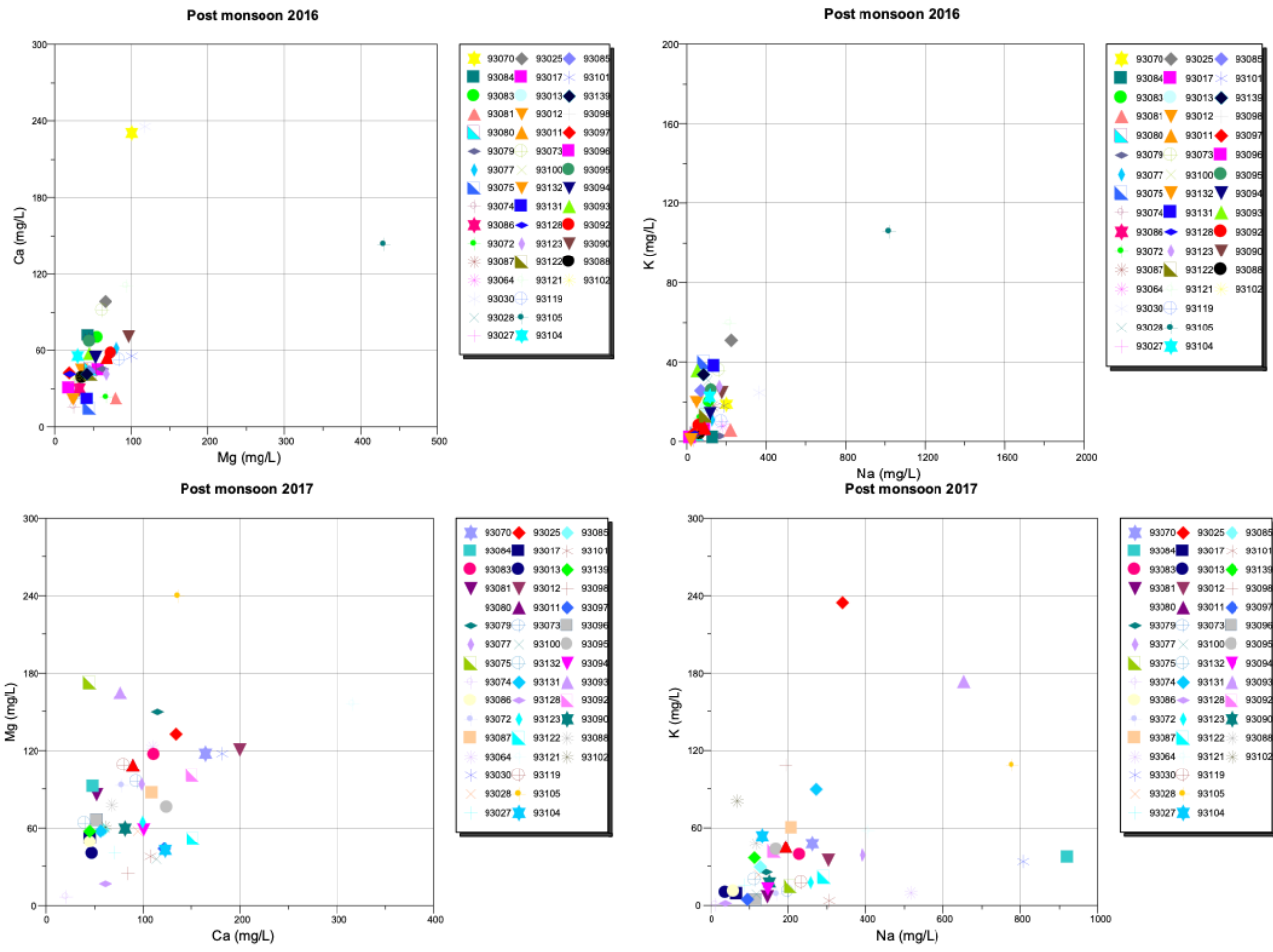


Figure 7

Scatter diagram for post-monsoon.

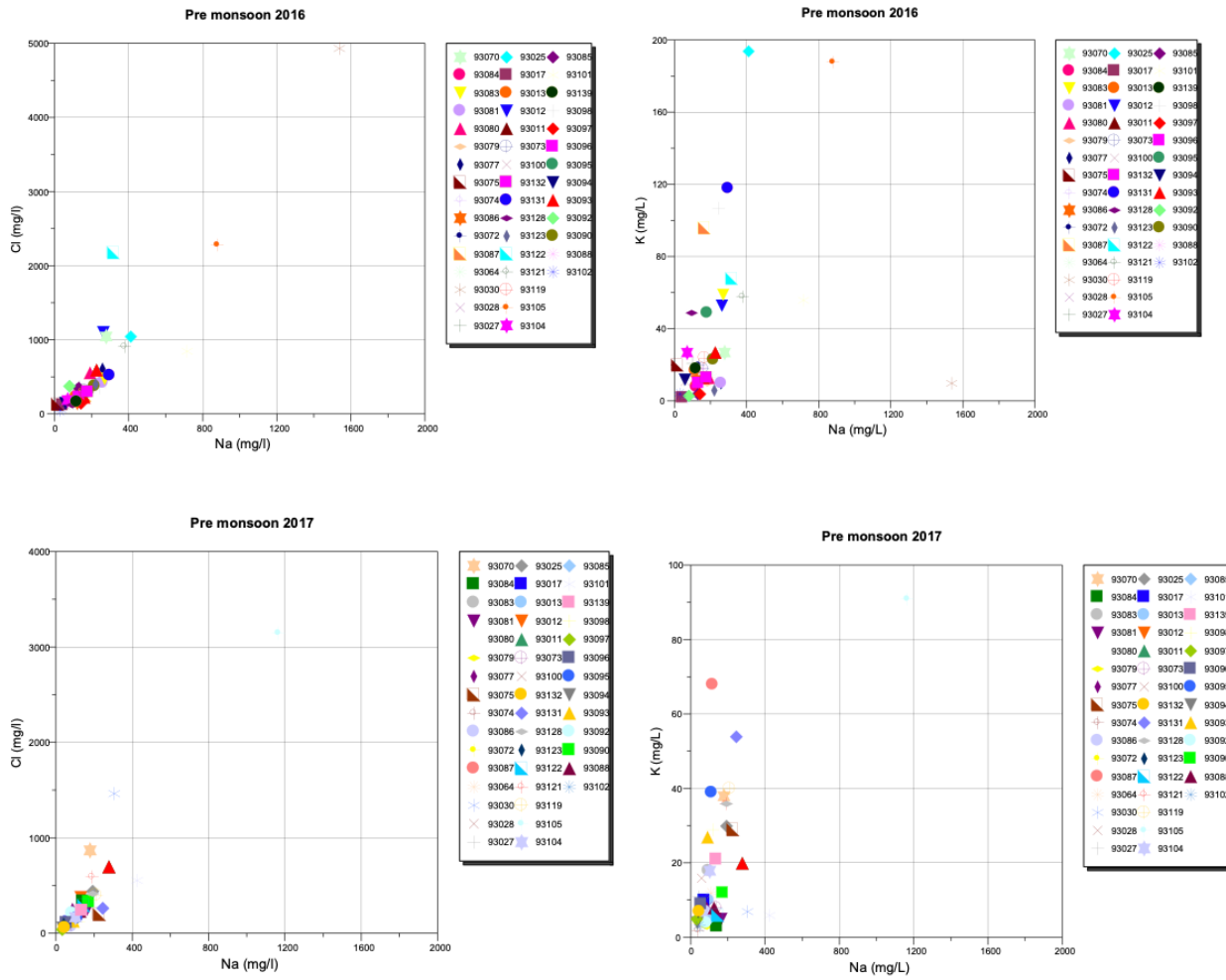


Figure 8
Scatter diagram for pre-monsoon season.

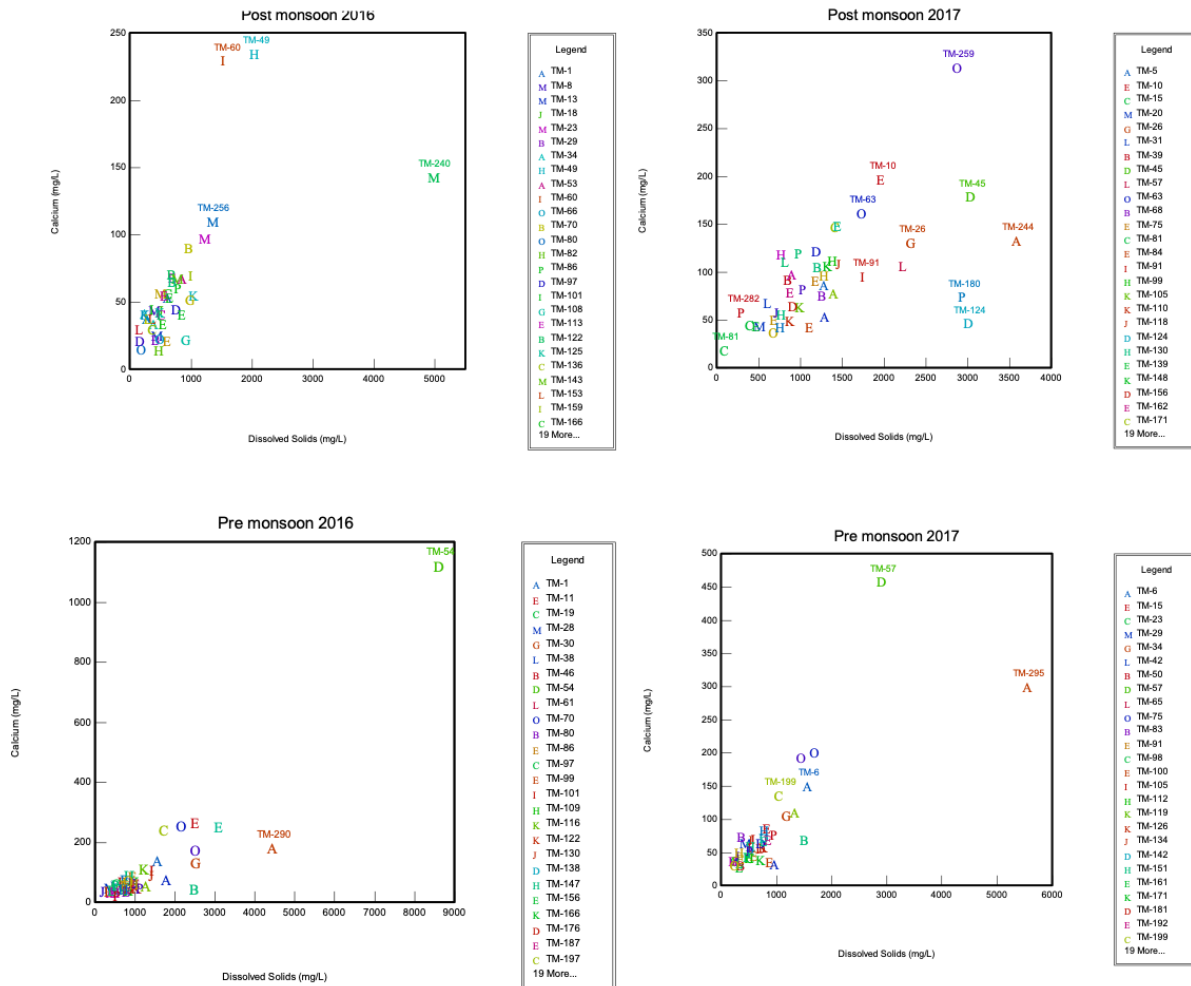


Figure 9

Cross plot representation of collected samples.

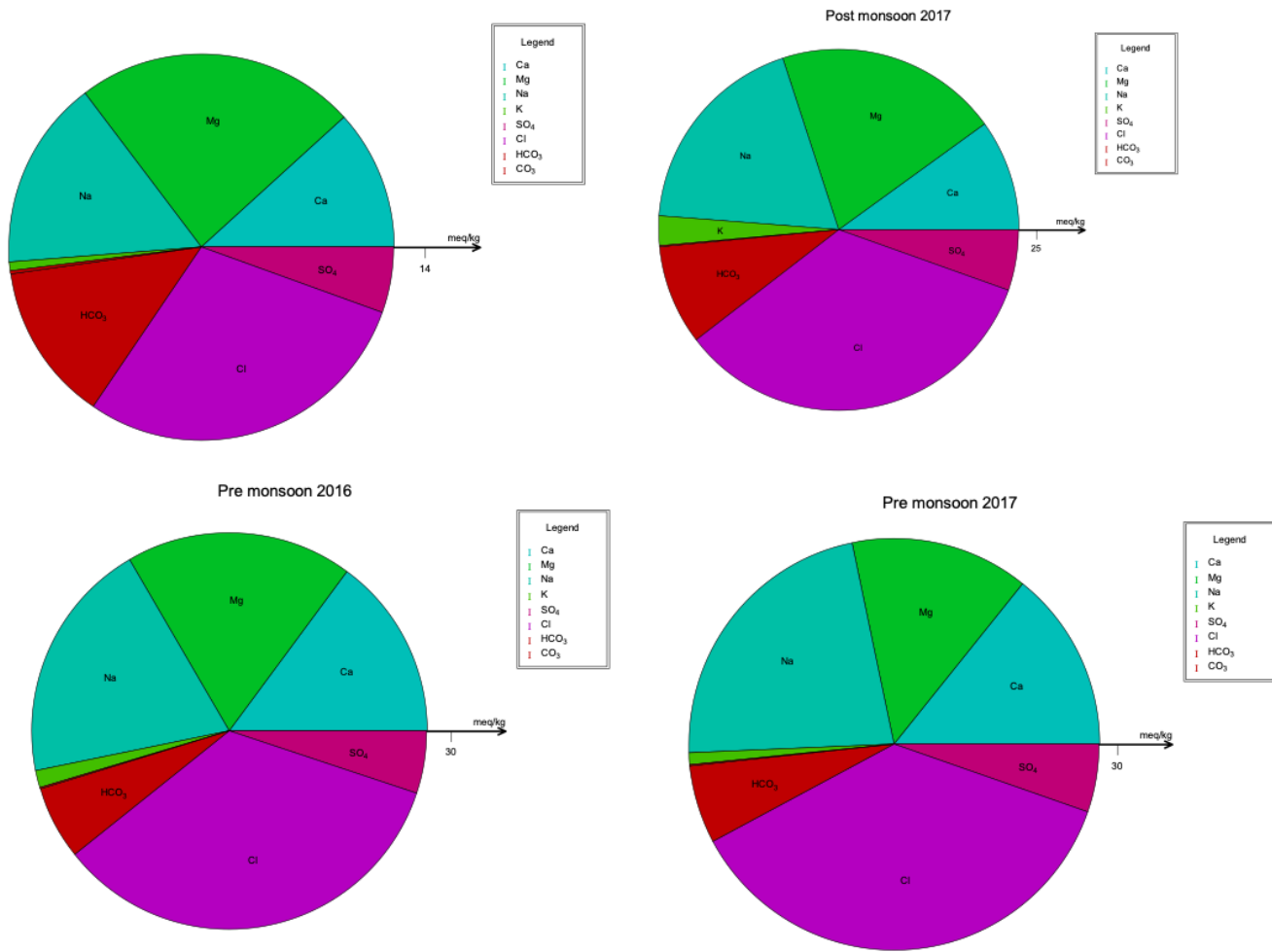


Figure 10

Pie chart for post and pre-monsoon

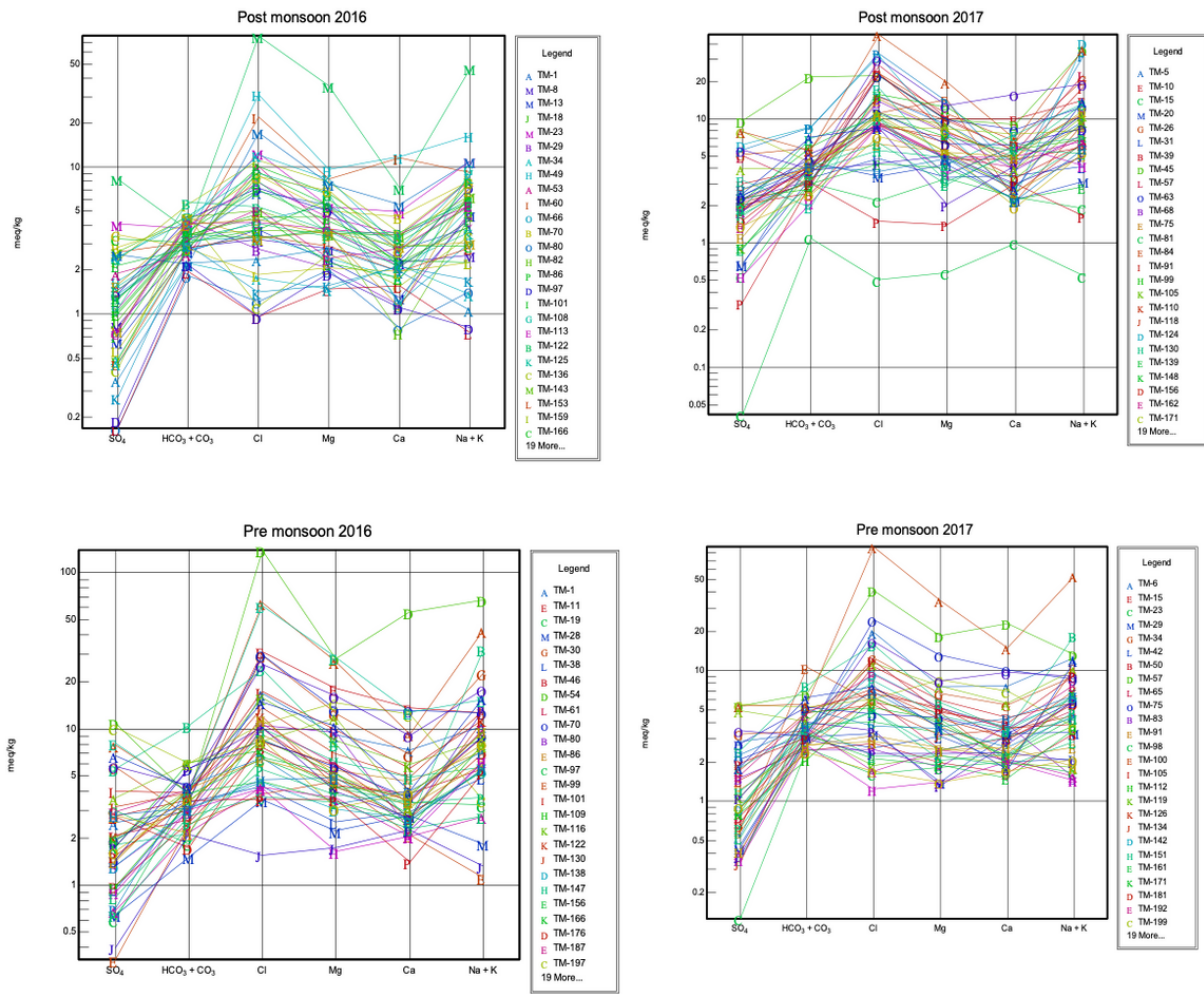


Figure 11

Schoeller diagram for post and pre-monsoon

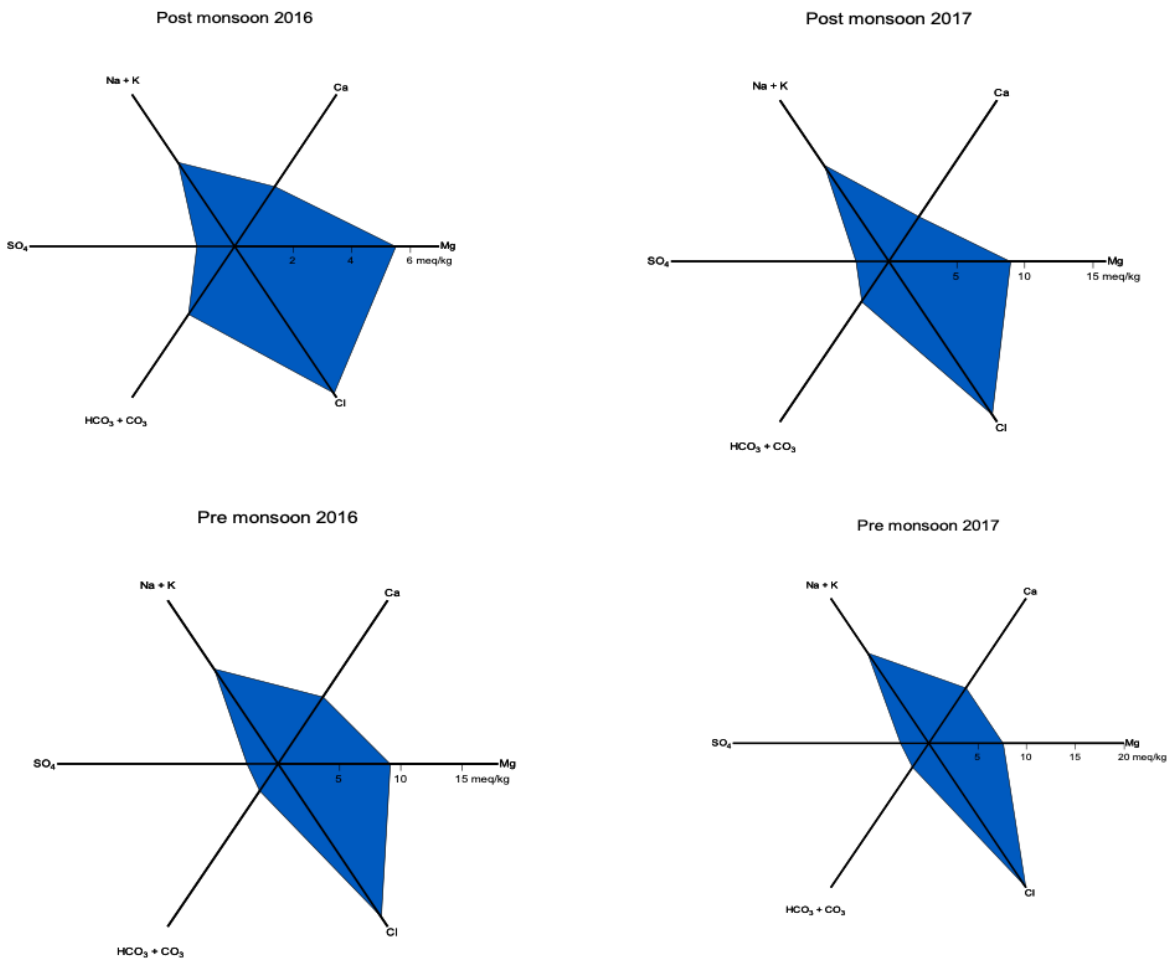


Figure 12

Radial plot for post and pre-monsoon