Global NEST Journal, Vol 18, No 3, pp 527-545, 2016

ASSESSMENT OF SEASONAL VARIATIONS IN SURFACE WATER QUALITY OF COOUM RIVER IN CHENNAI, INDIA – A STATISTICAL APPROACH

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Received: 08/10/2015
Accepted: 09/12/2015
Available online: 03/06/2016

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ABSTRACT

Rapid development in industrial sectors and population expansion has adverse impact on the *Cooum* river basin, especially Chennai region. The present study focuses on the assessment of seasonal variation in surface water quality of *Cooum* river basin. The samples were collected seasonally and are categorized as pre-monsoon, monsoon and post-monsoon during March 2013 to March 2014. Eighteen physicochemical parameters were assessed for eleven different samples collected along the channel of C*ooum* river basin. Statistical tools such as correlation analysis scatter plots, box plot and multivariate tools such as cluster analysis and principal component analysis were applied to categorize the *Cooum* river water quality. From the data sets, the ionic concentration, organic loads exhibits positive correlation (R^2>0.7) for all three seasons. Also, box plot and scatter plot results revealed that during post-monsoon season the ionic concentration along with organic and inorganic levels were slightly higher than monsoon and pre-monsoon. Similarly, multivariate statistical tools such as principle component analysis (PCA) indicate that the ionic concentrations and organic load contributed more than 50% of variance while cluster analysis (CA) reveals that nature of pollutant load among the sites.

Keywords: Seasonal variation, physicochemical characteristics, Surface water quality, Statistical analysis

1. Introduction

River plays a major role to systematize landscape and giving shape to the ecological setting of a basin. They also possess important role in controlling the global water cycle with active agents of transport (Garrels *et al.,* 1975; Kumarasamy *et al.,* 2014). Furthermore, the river carries substances either in dissolved or suspended form, from one point source to another based upon its physicochemical nature. Environmental factors such as rainfall, temperature, weathering of rocks, anthropogenic activities plays crucial task in quality of rivers. The major cause of rivers flowing through urban areas has been associated with water quality problems and the practice of discharging untreated industrial and domestic wastewater (Hall, 1984). Several studies have been conducted on different river basin based on the hydrology and geochemical variations (Shrestha and

Kazma, 2007; Kihampa *et al.*, 2013; Koklu *et al.*, 2010; Kumarasamy *et al.*, 2014; Singh *et al.*, 2005). Monitoring the surface runoff of a river on seasonal basis provides valuable information on the ecohydrological conditions of a river basin (Kumarasamy *et al.*, 2014).

Chennai is a metropolitan city in India, comprising many industries in and around the outskirts. The population in Chennai is accelerating day by day due to migration of people from various parts of villages and other areas in India. The river *Cooum* is the oldest river basin in Chennai and due to movement of population from rural to urban rapidly increases the pressure on the drainage system and sewage treatment plants, hence the discharge of these sewage in to *Cooum* makes it more polluted. Understanding the river quality is very important, as the chemical alteration of the groundwater depends on factors such as interaction with solid phases, residence time of groundwater, seepage of polluted river water and anthropogenic impacts (Umar *et al.*, 2006; Stallord and Demand, 1983; Faure, 1998). Giridharan *et al.*, (2008) reported the groundwater quality near the proximity of *Cooum* river analyzed for geochemical analysis. It has been identified that proximity areas near to the banks of the *Cooum* river were major source of ground water deterioration of these areas. In another study, the *Cooum* river has been analyzed from the origin till it reaches the ocean (48 km stretch) with different classification (such as upstream, middle and downstream) after tsunami restoration. However, in the usual practice, the pollutants from runoff due to various activities such as agricultural practice and other domestic practices get more intense pollution in the downstream of the river. Hence, in the present study, the seasonal variations in surface water quality of *Cooum* river especially Chennai region (downstream) was assessed to understand the level of pollution load in the river. Statistical analysis has been carried out in this study to reduce the range of uncertainty. In recent years of research, various statistical techniques such as multivariate statistical analysis through principal component analysis (PCA), cluster analysis (CA), have been used to evaluate and interpret complex datasets to better understand the river water quality (Fan *et al.,* 2010). Principle component analysis (PCA) used to explain overall association among the physicochemical parameters (Khimpa *et al.*, 2013).

Also, the other statistical techniques such as Boxplot, Scatter plot are widely accepted to determine the water quality (Krishnakumar *et al.*, 2014). These statistical tools have been used to explore data analysis for identify sampling points, pollution sources and most significant variable responsible for changes in river water (Aris *et al.*, 2012). Furthermore, statistical approaches have been employed to data recorded in several complex systems where data reduction and interpretation can be easily analyzed through application of statistical techniques. In addition, large range correlation can be achieved using statistical approaches which are means to interpret river water quality compared to conventional methods that infer without statistical significance.

2. Materials and Methods

2.1. Study area

River *Cooum* originates from Kesavaram dam, Kesavaram village at about 48 km west of Chennai. Though river *Cooum* originates from this dam, the excess water from the Cooum tank (79.82° latitude and 13.02° longitude) joins this course at about 8 km and this is considered as the head of the river *Cooum*. Throughout the river stretch in the upper part of the river, it was found that many agricultural activities are being carried out. The river receives a sizeable quantity of sewage from its neighborhood after it reaches Vanagram near Chennai. It flows through Kanchipuram, Thiruvallur and Chennai districts for a distance of about 68 km, after which it flow through the heart of the Chennai city and enters into the sea, Bay of Bengal. Eleven locations (Figure 1) have been identified to collect samples from the 18 km stretch of river basin in Chennai city.

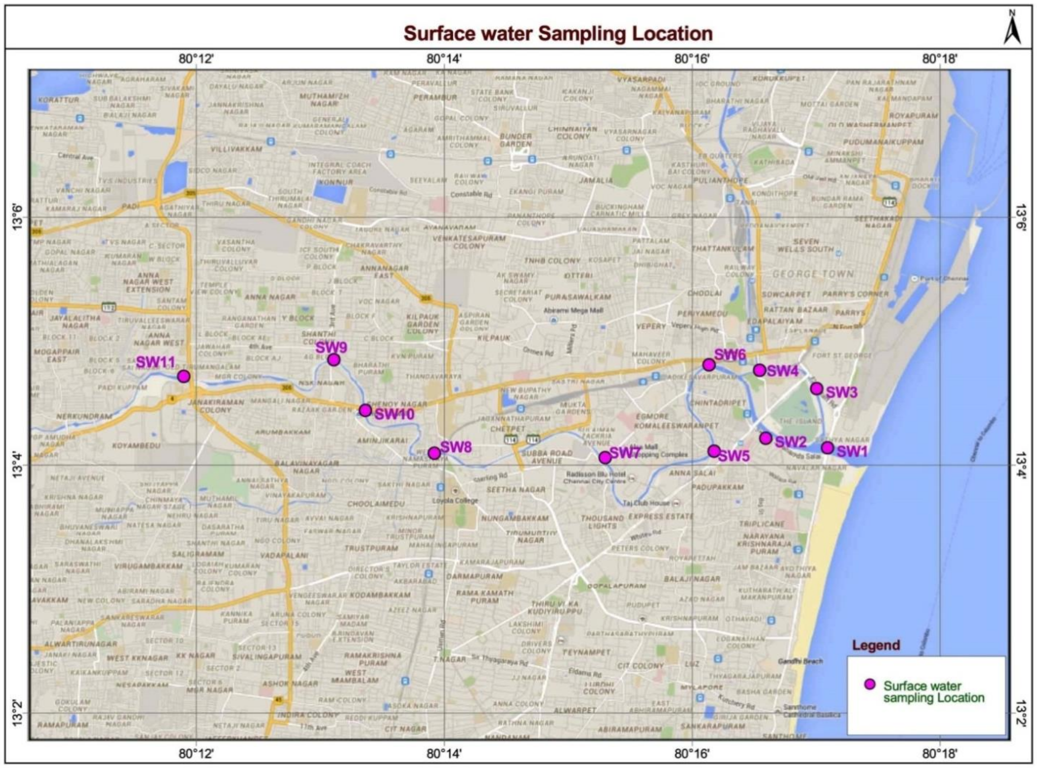


Figure 1. Overview of *Cooum* river and sampling locations

2.2. Methodology

Sample collection was carried out at each sampling site during March 2013-March 2014 (categorized as pre-monsoon, monsoon and post-monsoon). The sampling locations and their designation are presented in Table 1. Grab sampling procedure has been adopted as per the standards prescribed by CPCB (CPCB 2008) for collection of samples from the river. Samples were collected in pre-cleaned, sterilized polyethylene bottles and utmost care was taken to fill the bottles without air bubbles.

Table 1. Sampling points and designation

Sampling Location	Designation	Latitude	Longitude
Napier Bridge	SW1	13º04’07.77”N	80º17’04.22”E
Opposite flag house	SW2	13º04’12.36”N	80º16’34.33”E
Opposite New Secretariat	SW3	13º04’36.51”N	80º16’58.92”E
New jail cemetry	SW4	13º04’45.33”N	80º16’31.35”E
Chindadripet Bridge	SW5	13º04’06.16”N	80º16’09.22”E
Chitratalkies Bridge	SW6	13º04’48.05”N	80º16’06.86”E
Anderson bridge	SW7	13º04’03.01”N	80º15’16.55”E
Namasivayapuram causeway	SW8	13º04’05.26”N	80º13’53.69”E
Annanagar bridge	SW9	13º04’50.41”N	80º13’05.05”E
Aminjikarai bridge	SW10	13º04’25.85”N	80º13’20.33”E
Koyembedu bridge	SW11	13º04’42.34”N	80º11’52.37”E

The collected samples were labelled and taken into the laboratory using a refrigerator box. The reagents used in experimentation were prepared by using double distilled water. The samples were analyzed for eighteen parameters such as pH, Electrical conductivity (EC), Total dissolved solids (TDS), Dissolved Oxygen (DO), Ammonia-Nitrogen (NH_3), Nitrite (NO_2^-), Nitrate (NO_3^-), Sulphates (SO_4^{2-}), Chlorides (Cl^-), Potassium (K^+), Sodium (Na^+), Calcium (Ca^{2+}), Magnesium (Mg^{2+}), Carbonate (CO_3^{2-}), Bicarbonate (HCO_3^-), Chemical oxygen demand (COD), Biochemical oxygen demand (BOD), Phosphates (PO_4^{-3}). The physicochemical parameters are estimated by following standard procedure prescribed by American Public Health Association (APHA 2001). The parameters such as pH, EC were measured using potable kit (ELICO, India) at site during sampling. The analytical methods adopted for analysis of water quality parameters are presented in Table 2. The analytical data quality was ensured through standardization experiments with duplicates and average has been reported.

Table 2. Analytical methods used for determination of physicochemical parameters

S. no	Parameter	Abbreviations	Unit	Analytical method
1	pH	-	-	Potentiometric
2	Electrical Conductivity	EC	µs cm^{-1}	Potentiometric
3	Total dissolved solids	TDS	mg l^{-1}	Gravimetric
4	Dissolved oxygen	DO	mg l^{-1}	Winkler trimetric
5	Ammonical nitrogen	NH_4^+	mg l^{-1}	Spectrophotometry
6	Nitrite	NO_2^-	mg l^{-1}	Spectrophotometry
7	Nitrate	NO_3^-	mg l^{-1}	Spectrophotometry
8	Sulphate	SO_4^{2-}	mg l^{-1}	Nephelometry
9	Chloride	Cl^-	mg l^{-1}	Titrimetric
10	Potassium	K^+	mg l^{-1}	Flame photometric
11	Sodium	Na^+	mg l^{-1}	Flame photometric
12	Calcium	Ca^{2+}	$CaCO_3$ mg l^{-1}	Titrimetric
13	Magnesium	Mg^{2+}	$CaCO_3$ mg l^{-1}	Titrimetric
14	Carbonate	CO_3^{2-}	mg l^{-1}	Titrimetric
15	Bicarbonate	HCO_3^-	mg l^{-1}	Titrimetric
16	Chemical oxygen demand	COD	mg l^{-1}	Open reflux method
17	Biochemical oxygen demand	BOD	mg l^{-1}	Titrimetric
18	Phosphates	PO_4^{-3}	mg l^{-1}	Spectrophotometry

2.3. Statistical analysis

The application of statistical tools helps in interpretation of complex data matrices to understand the water quality, identification of possible sources that influence water systems and offers valuable information for reliable management of water resources (Simeonov *et al.*, 2004, Reghunath *et al.*, 2002). In this study, the exploratory data analysis such as Boxplot designs, Scatterplot, multivariate statistical analysis such as Principle component analysis (PCA), Cluster analysis (CA) were carried out using Minitab software and correlation matrix were carried out using SPSS. The PCA was performed on experimental data (raw data) using the correlation matrix as the methods of classification used here are non-parametric and they make no assumptions about the underlying statistical distribution of the data and therefore no evaluation of normal (Gaussian) distribution of the data is necessary. The Characterization roots (Eigen values) of the PCs (principle components) are a measure of their associated variances and the sum of variances coincides with total number of variables. These correlations of PCs are given by loading plot and individual observation transformations are called score plots. Cluster analysis (CA) helps to delineate variables, observations based on its characteristics (Shrestha and Kazama, 2007).The Euclidean distance yields similarity between samples and a distance can be estimated by difference between analytical values from the samples. In this study, Hierarchical agglomerative CA was performed based on the normalized data by means of ward method using squared Euclidean distances as a measure of similarity. The spatial variability of water quality was determined from CA, using linkage distance. Cluster analysis was used in the study as a visual summary of intra relationship amongst variations parameters to better understanding of governing factors (Pejman *et al.*, 2009). Likewise, PCA provides information on parameters that describe whole data set with minimum loss of original information. It also explains the variances of large set of inter correlated variables and transforms to uncorrelated principal components. The correlation between the parameters was carried out by Pearson's correlation. A correlation analysis is a bivariate method applied to describe the degree of relationship between hydrochemical parameters. Variable representing with correlation coefficient is *r* and independent variables are the percentage of variance with dependent variable. A high correlation coefficient (near to 1 or -1) implies a good relationship between two variables and zero implies there is no relationship between variables (Venkatramanan *et al.*, 2013). Scatter plots were employed in order to illustrate the relationship among parameters based on seasonal variation, while, box plot helps to assess and compare distributions.

3. Results and Discussion

3.1. Physicochemical analysis

The various physicochemical characteristics such as pH, Electrical conductivity (EC), Total dissolved solids (TDS), Dissolved Oxygen (DO), Ammonia-Nitrogen (NH_3), Nitrite (NO_2^-), Nitrate (NO_3^-), Sulphates (SO_4^{2-}), Chlorides (Cl^-), Potassium (K^+), Sodium (Na^+), Calcium (Ca^{2+}), Magnesium (Mg^{2+}), Carbonate (CO_3^{2-}), Bicarbonate (HCO_3^-), Chemical oxygen demand (COD), Biochemical oxygen demand (BOD), Phosphates (PO_4^{3-}) were analysed for the samples collected from different sampling points of *Cooum* river during pre-monsoon, monsoon and post-monsoon and the results along with minimum, maximum, mean and standard deviation are presented in Table 3, Table 4 and Table 5, respectively.

Though the seasonal variation in quality of surface water of *Cooum* is depicted in Table 3, Table 4 and Table 5, for the sake of brevity, only TDS and EC Scatter plots have been presented in Fig 2a and Fig 2b, respectively. It can be noted that the pH value of samples from various locations are in the range of 7.3-7.9 with a mean of 7.6 during pre-monsoon (Table 3). Similarly, during monsoon season the pH was in neutral ranging from 7.0-7.4 with a mean of 7.2 which is slightly lower than pre-monsoon season (Table 4). However, during post monsoon, the pH was found out to be slightly alkaline ranging from 7.3-8.1 with a mean of 7.6 (Table 5).

Electrical conductivity (Fig. 2a) during pre-monsoon ranges from 1696 to 14160 µS cm^{-1} with mean of 4073 µS cm^{-1} and during the monsoon season, the electrical conductivity ranges from 1510- 7140 with mean of 3194 µS cm^{-1} which is low compared to other season. However, during post-monsoon season the EC was very high in the range of 2260-42400 µS cm^{-1} with mean of 10560 µS cm^{-1}, which may be due to large contact time of back water intrusion. The concentration of total dissolved solids (TDS) (Fig. 2b) during pre-monsoon season was in the range of 1103 mg l^{-1} to 9820 mg l^{-1} with mean of 2793 mg l^{-1}, whereas, during monsoon season, the range was 920 mg l^{-1} to 4385 mg l^{-1} with mean of 1937.5 mg l^{-1}. Further, it can be noted that during post-monsoon season the values ranges from 1380 to 25520 mg l^{-1} with mean of 6377 mg l^{-1}. The dissolved oxygen concentration in the river is nil expect for sampling location SW1 for all the three seasons, which indicates that other sites are prone to anthropogenic risks (Table 3, Table 4, Table 5). The reason for DO concentration at SW1 alone would be due to backwater as the site is located near to the Bay of Bengal. BOD and COD analyses were carried out and it can be noted that COD values were in the range of 113-376 mg l^{-1} with mean of 252 mg l^{-1} during pre-monsoon (Table 3). During monsoon season, the values were found out to be low in the range of 102-236 mg l^{-1} with mean of 183 mg l^{1} (Table 4).

Table 3. Physicochemical parameters of surface water in *Cooum* river during pre-monsoon season

Sam.pts	Pre-monsoon																	
	Physicochemical parameters																	
	pH	**EC**	**TDS**	**DO**	**NH_3**	**NO_2^-**	**NO_3^-**	**SO_4^{2-}**	**Cl^-**	**K^+**	**Na^+**	**Ca^{2+}**	**Mg^{2+}**	**CO_3^{2-}**	**HCO_3^-**	**COD**	**BOD**	**PO_4^{3-}**
SW1	7.7	14160	9820	3.8	17.8	0	1	4210	4829	136	4803	132	255	-	340	354	124	1.8
SW2	7.6	3925	2775	0	14.6	0.1	0	1470	973	74	1331	56.1	76	-	430	264	92	1.9
SW3	7.9	9100	6270	0	16	2.5	1.4	4360	2920	106	3173	104	98	-	400	284	98	1.9
SW4	7.5	2034	1456	0	18.5	1.4	0	710	587	47	678	40	68	-	390	218	75	1.7
SW5	7.6	3876	2740	0	17.2	0.5	1	1020	933	57	1107	48	102	-	440	246	85	2
SW6	7.3	1806	1230	0	18.4	4.4	1.1	864	316	24	296	184	116	-	424	113	35	2.9
SW7	7.4	1810	1240	0	18.2	0.15	0	820	312	25	358	220	76	-	432	161	43	0.8
SW8	7.7	2028	1380	0	11	0	2.2	650	356	26	310	244	84	-	440	129	36	0.8
SW9	7.4	1696	1103	0	16.5	0.2	0	280	308	21.3	305	80	27	-	200	272	92	2.4
SW10	7.6	1846	1119	0	18	0.4	0	320	328	23	312	88	24	-	194	360	124	2.7
SW11	7.5	2520	1644	0	13	0.15	0.1	570	422	24.4	432	124	34	-	228	376	128	3.8
Min.	7.3	1696	1103	0	11	0	0	280	308	21.3	296	40	24	NA	194	113	35	0.8
Max.	7.9	14160	9820	3.8	18.5	0.1	2.2	4360	4829	136	4803	244	255	NA	440	376	128	3.8
Mean	7.6	4073	2797.9	.34	16.3	.891	.618	1388.5	1116.73	51.24	120.00	87.22	1191.36	NA	356.18	252.4	84.72	2.06
S.D	0.168	3983.7	2776.5	1.14	2.46	1.39	0.76	1468.9	1448.9	39.03	69.41	63.56	1472.05	NA	100.15	91.06	34.53	0.87

***NA-**Not applicable**; *BDL-**Below detectable limit

Table 4. Physicochemical parameters of surface water in *Cooum* river during monsoon season

Sam.pts	Monsoon																	
	Physicochemical parameters																	
	pH	**EC**	**TDS**	**DO**	**NH_3**	**NO_2^-**	**NO_3^-**	**SO_4^{2-}**	**Cl^-**	**K^+**	**Na^+**	**Ca^{2+}**	**Mg^{2+}**	**CO_3^-**	**HCO_3^-**	**COD**	**BOD**	**PO_4^{3-}**
SW1	7	7140	4385	4.2	14.2	BDL	BDL	815	1529	75	1402	112	140	-	306	182	64	1.1
SW2	7.2	4580	2852	1.1	12	BDL	BDL	630	772	50	760	36	82	-	240	164	52	1.2
SW3	7.2	6720	3842	0.8	13	BDL	BDL	785	1138	70	1173	85	99	-	310	156	50	0.9
SW4	7.4	3486	2024	0.7	16.2	BDL	BDL	453	440	38	540	52	58	-	340	160	84	2.1
SW5	7.3	3520	2290	0.3	19	BDL	BDL	635	584	41	641	42	64	-	280	196	68	2.5
SW6	7.1	1642	1030	0.4	17.2	BDL	BDL	154	212	10	208	88	54	-	294	102	32	0.9
SW7	7.4	1650	1052	0.8	18	BDL	BDL	185	140	18	158	140	32	-	384	140	40	0.2
SW8	7.4	1550	924	0.2	12	BDL	BDL	140	156	17	180	144	28	-	240	204	72	1.9
SW9	7.2	1510	920	0.4	14	BDL	BDL	190	200	17	210	77	22	-	192	224	72	2.2
SW10	7.3	1650	972	0.3	12	BDL	BDL	280	190	14	212	72	20	-	176	236	75	2.1
SW11	7.3	1686	1022	0.2	9	BDL	BDL	270	200	17	212	78	28	-	188	250	85	1.8
Min.	7.0	1510	920	0.2	9	NA	NA	140	140	10	208	36	20	NA	176	102	32	0.2
Max.	7.4	7140	4385	4.2	19	NA	NA	815	1529	75	1402	144	140	NA	340	236	85	2.5
Mean	7.2	3194	1937.5	0.85	14.2	NA	NA	412.4	505.5	33.36	517.8	84.2	57	NA	268.18	183.09	63.09	1.53
S.D	0.13	2123.80	1265.93	1.14	3.05	NA	NA	260.65	464.45	23.22	436.66	35.85	37.73	NA	66.98	44.3	17.42	0.714

***NA-**Not applicable; ***BDL**-Below detectable limit

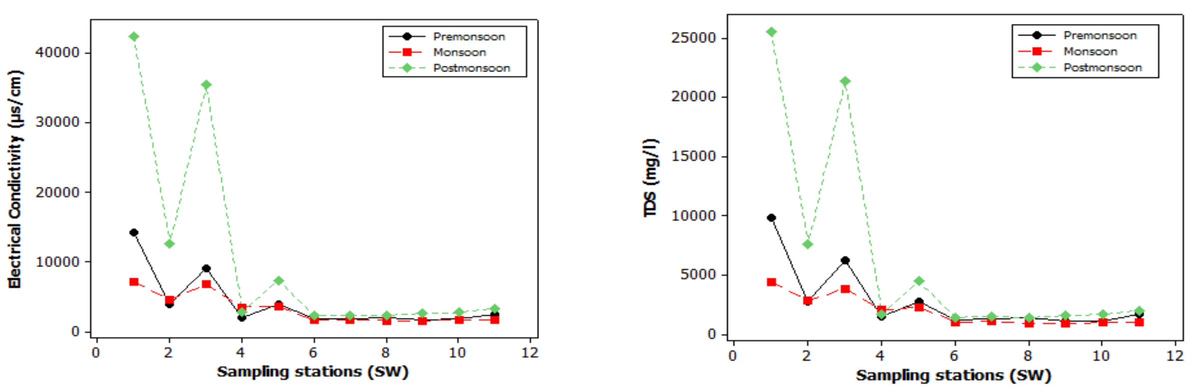
Table 5. Physicochemical parameters of surface water in *Cooum* river during Post-monsoon season

Sam.pts	Post-monsoon																	
	Physicochemical parameters																	
	pH	**EC**	**TDS**	**DO**	**NH_3**	**NO_2^-**	**NO_3^-**	**SO_4^{2-}**	**Cl^-**	**K^+**	**Na^+**	**Ca^{2+}**	**Mg^{2+}**	**CO_3^{2-}**	**HCO_3^-**	**COD**	**BOD**	**PO_4^{3-}**
SW1	8.1	42400	25520	4.6	18	0	2.5	6660	8589	227	9110	472	43	0	549	396	128	3.1
SW2	7.6	12600	7580	0	14	0.18	0	1850	2854	145	2740	368	24	0	539.24	216	68	6.8
SW3	7.5	35500	21360	0	16	0	2.9	4360	10147	207	9250	448	29	0	500.2	124	36	2.4
SW4	7.4	2780	1692	0	20	0	1.4	1710	1289	43	1155	593	38	0	463.6	212	66	6
SW5	7.5	7320	4460	0	11	0.28	1.78	1020	1425	55	1315	248	24	0	531.92	236	77	4.9
SW6	7.3	2330	1420	0	18	0	1.1	864	460	54	466	424	34	0	539.24	248	81	5.1
SW7	7.5	2360	1490	0	17	0.19	0	820	480	34	520	176	15	0	519.72	222	72	7.9
SW8	7.4	2260	1380	0	15	0	1.9	780	410	57	405	208	43	0	536.8	236	76	8
SW9	7.5	2600	1592	0	16.2	0.29	0	885	430	27	405	216	34	0	312.32	266	88	7.9
SW10	7.5	2700	1642	0	15.4	0.19	0	790	420	31	455	193	32	0	351.36	320	110	5.7
SW11	7.7	3320	2012	0	13.6	0.22	0	970	600	36	575	254	37	0	287.92	348	120	7.3
Min.	7.3	2260	1380	0	11	0	0	780	410	27	405	208	15	NA	287.92	124	36	3.1
Max.	8.1	42400	25520	0	20	0.29	2.9	6660	10147	227	9250	593	43	NA	549	396	128	8
Mean	7.6	10560.9	6377.09	0.42	15.83	0.12	1.05	1882.64	2464	83.27	2399.64	327.27	32.09	NA	466.48	256.72	83.81	5.91
S.D	0.21	14465.1	8693.73	1.38	2.467	0.12	1.11	1901.05	3508.8	73.69	3422.54	140.11	8.58	NA	99.75	74.32	26.60	1.92

***NA-**Not applicable; ***BDL-**Below detectable limit

Contrary, the post-monsoon season mean value was found to be 256 mg l^{-1} which is higher compared with other two seasons (Table 5). Similarly for BOD, the mean values of pre-monsoon and post monsoon were same but slight decrease was observed for monsoon season indicating rainfall effect of decrease in organic load values. Nitrogen species such as ammonia, nitrate, nitrites were estimated. It can be observed that during pre-monsoon season, the concentration of NH_3, NO_2^-, NO_3^-, were in the range from 11-18.5 mg l^{-1}, 0 - 0.1 mg l^{-1}; 0-2.2 mg l^{-1} with mean values of 16.3, 0.891 and 0.618 mg l^{-1} respectively (Table 3). Similarly, during monsoon season only ammoniacal nitrogen presence was detected ranging from 9-19 mg l^{-1} with mean of 14.2 mg l^{-1} (Table 4). Other species of nitrogen were found to be below detectable limit indicating inhibition of nitrification by microorganism. Likewise, the post-monsoon with mean value of 15.83 mg l^{-1} were found to be similar with pre-monsoon trend (Table 5). Phosphates (PO_4^{3-}) values ranges from 0.8 - 3.8 mg l^{-1}, 0.2 - 2.5 mg l^{-1}, 3.1-8 mg l^{-1} during pre-monsoon, monsoon and post-monsoon seasons. It can be noted that the post-monsoon values (Table 5) were higher when compare to other seasons indicating less runoff of river and more anthropogenic activities.

During the pre-monsoon season, the concentration of cations such as Ca^{2+},Mg^{2+},Na^{+},K^{+} ions ranges from 40 - 244 mg l^{-1}, 24 - 255 mg l^{-1}, 296 - 4803 mg l^{-1} and 21.3 – 136 mg l^{-1} with mean value of 87.22, 1191.36, 120 and 51.24 mg l^{-1}, respectively (Table 3).The order of abundance were found to be Na^{2+}>Mg^{2+}>Ca^{2+}>K^{+}. However, during monsoon season, the cations were in the range of 20 - 140 mg l^{-1}, 208 – 1402 mg l^{-1}, 10 – 75 mg l^{-1} and 36- 144 mg l^{-1} with mean of 84.2, 57, 517.8 and 33.36 mg l^{-1} (Table 4). Similarly, during the post-monsoon season, the value ranges from 208 – 593 mg l^{-1}, 15 –43 mg l^{-1}, 405 – 9250 mg l^{-1} and 27 - 227 mg l^{-1} with mean of 140.11, 8.58, 3422.54 and 73.69 mg l^{-1}. The order of abundance were Na^{2+}>Mg^{2+}>Ca^{2+}>K^{+}. Despite, the concentration of ions in the monsoon and post-monsoon were different from each other. It can be noted that the order of abundance were similar for pre-monsoon and post-monsoon compared with monsoon. The anionic concentrations such as HCO_3^-, SO_4^{2-}, Cl^- were quantified and the results are presented in Table 3 Table 4, Table 5 respectively. During pre-monsoon season the concentration of anions ranges from 194 – 440 mg l^{-1}, 280 – 4360 mg l^{-1} and 380 – 4829 mg l^{-1} with mean of 100.15, 1468.9 and 1448.90 mg l^{-1} (Table 3). The order of abundance was observed as SO_4^{2-}>Cl^->HCO_3^-. The monsoon anionic concentration ranges from 176-340 mg l^{-1}, 140- 815 mg l^{-1} and 140 - 1529 mg l^{-1} with mean of 268.18, 412.4 and 505.5 mg l^{-1} (Table 4). Likewise, during post-monsoon season, the concentration ranges from 287.92 - 549 mg l^{-1}, 780 - 6660 mg l^{-1} and 410 - 10147 mg l^{-1} with mean of 356.16, 1882.64 and 3508.8 mg l^{-1} (Table 5). It can be noted that concentration was different in monsoon compared to post-monsoon values. However, the order of abundance was similar with monsoon and post-monsoon values exhibiting Cl^-> SO_4^{2-}> HCO_3^-.



(a) (b)

Figure 2. Scatter plot for all sampling points with seasonal variation for (a) EC and (b) TDS

3.2. Statistical analysis

3.2.1. Boxplot design

The box plot or box whisker plots of all parameters with seasonal variation are presented in Figures 3 and 4.The EC (Fig.3b) and TDS (Fig.3c) plots were almost similar to each other, but during post-monsoon, the concentration is slightly high compared to other seasons. This may be due to the fact that more of evaporation of water. This shows that increasing level of EC can enhance ionized substances of water (Elangovan *et al.*, 2013). The DO levels were found to be low in seasons, pre-monsoon and post-monsoon. However, during monsoon seasons the concentration was slightly higher indicating that rainfall droplets contain dissolved oxygen from atmosphere. The trend observed for various parameters such as COD (Fig. 3d), BOD (Fig. 3e), NH_3 (Fig. 3f), NO_2^- (Fig. 3g) and NO_2^- (Fig. 3h) indicates the presence of high load of dissolved organic and inorganic matter present in *Cooum* river due to which the river is polluted extremely by the release of sewage and other effluents discharged at the upstream of various stations. This is attributed to anaerobic condition of the river which in turn responsible for ammonia and organic acid formation (Shrestha and Kazame 2007).

Similarly, it can be noted that ionic concentrations such as SO_4^{2-} (Fig. 4a), Cl^- (Fig. 4b), K^+ (Fig. 4c), Na^+ (Fig. 4d), Mg^{2+} (Fig. 4e), Ca^{2+} (Fig. 4f), PO_4^{3-} (Fig. 4g) and HCO_3^- (Fig. 4h) of the *Cooum* river was high in post-monsoon season compared to other two seasons.

3.2.2.Correlation studies

The correlation coefficient values exhibiting +1 or -1 between variables reveals that there is strong correlation. However, zero value indicates that there is no relationship between them. The geochemical parameters showing correlation >0.7 are strongly correlated and 0.5-0.7 shows moderate correlation. The amount of variation in the dependent variable that is accounted by variation on the predicted variable is measured by the value of coefficient of determination (Adjusted R^2). The correlation matrix estimated for all three seasons are depicted in the Tables 6, 7 and 8. It can be noted from Table 6 that during pre-monsoon season EC and TDS were strongly correlated with major cations and anions. Likewise, SO_4^{2-} were strongly correlated with Cl^-, K^+, Na (R^2 >0.93). Cl^- were strongly correlated with K^+, Na^+ (R^2>0.95). The positive correlation during pre-monsoon may be due to long residence time of river water such that interaction of water and rock phenomenon may be initiated. The saline water intrusion from the near sea may also play a major role in increasing in the concentration of ions. During all the seasons, Na and Cl had a strong positive correlation. It is therefore, postulates that concurrent increase/decrease in the composition of ion in this river may be due to result of dissolution/ precipitation reaction and concentration effects. TDS and EC are positively correlated because conductance of electric current depends upon dissolved ionic species. Hence high EC concentration corresponds to High TDS (Siosemarde *et al.*, 2010).

3.2.3.Multivariate tools

Cluster analysis helps to detect spatial similarity among grouping sites of inter monitoring network (Singh *et al.*, 2005). The dendrogram for all three seasons viz., pre-monsoon, monsoon, post-monsoon are presented in Figure 5. It can be observed for pre-monsoon season (Figure 5a), Cluster 1 comprises of sites 1, 3 showing distance of 31.02 indicating high loads of pollutants, Cluster 2 comprises of sites 2, 5, 4, 9, 10, 11 with distance of 29.27 indicating moderate loads of physicochemical parameters, Cluster 3 comprises sites of 6, 7, 8 with distance of 27.82 indicating less polluted levels in the river *Cooum*. During monsoon season shown in Figure 5b, Cluster 1 comprises of sites 1, 2, 3, 4, 5 with relative distance of 46.47, Cluster 2 comprises of sites 6, 7 with distance of 10.93, Cluster 3 comprises of sites 8-11 with a distance of 9.32. During monsoon season, all the sampling points exhibited relatively less pollution load compared to other season which is due to the amount of rainfall received during the monsoon season. Similarly, post-monsoon results were shown in Figure 5c. and it can be noted that Cluster 1 and Cluster 3 comprises sites 1 and 3 with same distance value of 50.1 indicating high pollution loads compared to cluster 2 which is due to anthropogenic activities.

Table 6 Correlation coefficients among various surface water physicochemical parameters during pre-monsoon season

Parameters	pH	EC	TDS	DO	NH_4^+	SO_4^{2-}	Cl^-	K^+	Ca^{2+}	Mg^{2+}	Na^+	HCO_3^{2-}	COD	BOD	PO_4^{3-}
pH	1														
EC	.636*	1													
TDS	.634*	1.0**	1												
DO	.268	.840**	.839**	1											
NH_4	-.339	.121	.123	.203	1										
SO_4	-.187	-.042	-.040	-.212	.363	1									
Cl	.502	.322	.324	.166	-.406	.264	1								
K	.702*	.942**	.942**	.637*	.104	.154	.386	1							
Na	.622*	.998**	.998**	.850**	.155	-.028	.310	.939**	1						
Ca	.681*	.954**	.958**	.720*	.134	-.017	.265	.938**	.952**	1					
Mg	-.126	-.086	-.090	.057	-.302	.085	.493	-.04	-.090	-.254	1				
HCO_3	.304	.836**	.843**	.875**	.224	.097	.447	.732*	.842**	.779**	.172	1			
COD	.646*	.996**	.997**	.814**	.149	-.024	.294	.953**	.996**	.974**	-.137	.823**	1		
BOD	.148	.099	.118	-.054	-.022	.288	.491	.236	.096	.250	.272	.390	.132	1	
PO_4	.355	.427	.415	.370	.004	-.421	-.394	.288	.413	.368	-.536	.012	.413	-.704*	1

*Significant at 0.05 level, ** Significant at 0.01 level

Table 7. Correlation coefficients among various surface water physicochemical parameters during monsoon season

Parameters	pH	EC	TDS	DO	NH_4^+	SO_4^{2-}	Cl^-	K^+	Ca^{2+}	Mg^{2+}	Na^+	HCO_3^-	COD	BOD	PO_4^{3-}
pH	1														
EC	-.541	1													
TDS	-.558	.997**	1	.											
DO	-.655*	.722*	.745**	1											
NH_4	.035	-.007	.021	.032	1										
SO_4	-.450	.954**	.961**	.611*	.033	1									
Cl	-.642*	.984**	.989**	.810**	-.018	.932**	1								
K	-.473	.992**	.992**	.704*	.005	.966**	.972**	1							
Na	-.584	.995**	.997**	.759**	.007	.955**	.994**	.988**	1						
Ca	.101	-.167	-.178	.194	-.009	-.380	-.117	-.187	-.167	1					
Mg	-.672*	.953**	.964**	.819**	.112	.887**	.970**	.931**	.962**	-.107	1				
HCO_3	.066	.352	.353	.310	.696*	.260	.291	.352	.318	.278	.419	1			
COD	.219	-.236	-.236	-.151	-.617*	-.115	-.186	-.188	-.196	-.110	-.374	-.781**	1		
BOD	.361	-.128	-.137	-.102	-.445	-.018	-.124	-.072	-.099	-.248	-.254	-.506	.817**	1	
PO_4	.269	-.256	-.251	-.341	-.150	-.075	-.245	-.203	-.210	-.483	-.338	-.599	.679*	.807**	1

*Significant at 0.05 level, ** Significant at 0.01 level

Table 8. Correlation coefficients among various surface water physicochemical parameters during post-monsoon season

Parameters	pH	EC	TDS	DO	NH_4^+	SO_4^{2-}	Cl^-	K^+	Ca^{2+}	Mg^{2+}	Na^+	HCO_3^-	COD	BOD	PO_4^{3-}
pH	1														
EC	.690*	1													
TDS	.690*	1.000**	1												
DO	.870**	.730*	.730*	1											
NH_4	-.019	.137	.137	.291	1										
SO_4	.002	-.423	-.423	-.333	-.640*	1									
Cl	.180	.685*	.685*	.431	.142	-.677*	1								
K	.749**	.972**	.972**	.833**	.296	-.493	.667*	1							
Na	.548	.976**	.976**	.579	.154	-.462	.716*	.926**	1						
Ca	.613*	.962**	.962**	.647*	.108	-.475	.645*	.921**	.948**	1					
Mg	.609*	.991**	.991**	.650*	.173	-.465	.709*	.955**	.996**	.958**	1				
HCO_3	.143	.483	.483	.343	.597	-.685*	.527	.574	.527	.526	.525	1			
COD	.256	.175	.174	.421	.314	-.509	.366	.298	.120	.133	.152	.332	1		
BOD	-.001	.363	.363	.274	.112	-.527	.567	.345	.347	.481	.357	.353	-.176	1	
PO_4	.675*	.070	.070	.622*	-.001	.166	-.224	.191	-.114	-.040	-.037	-.164	.466	-.352	1

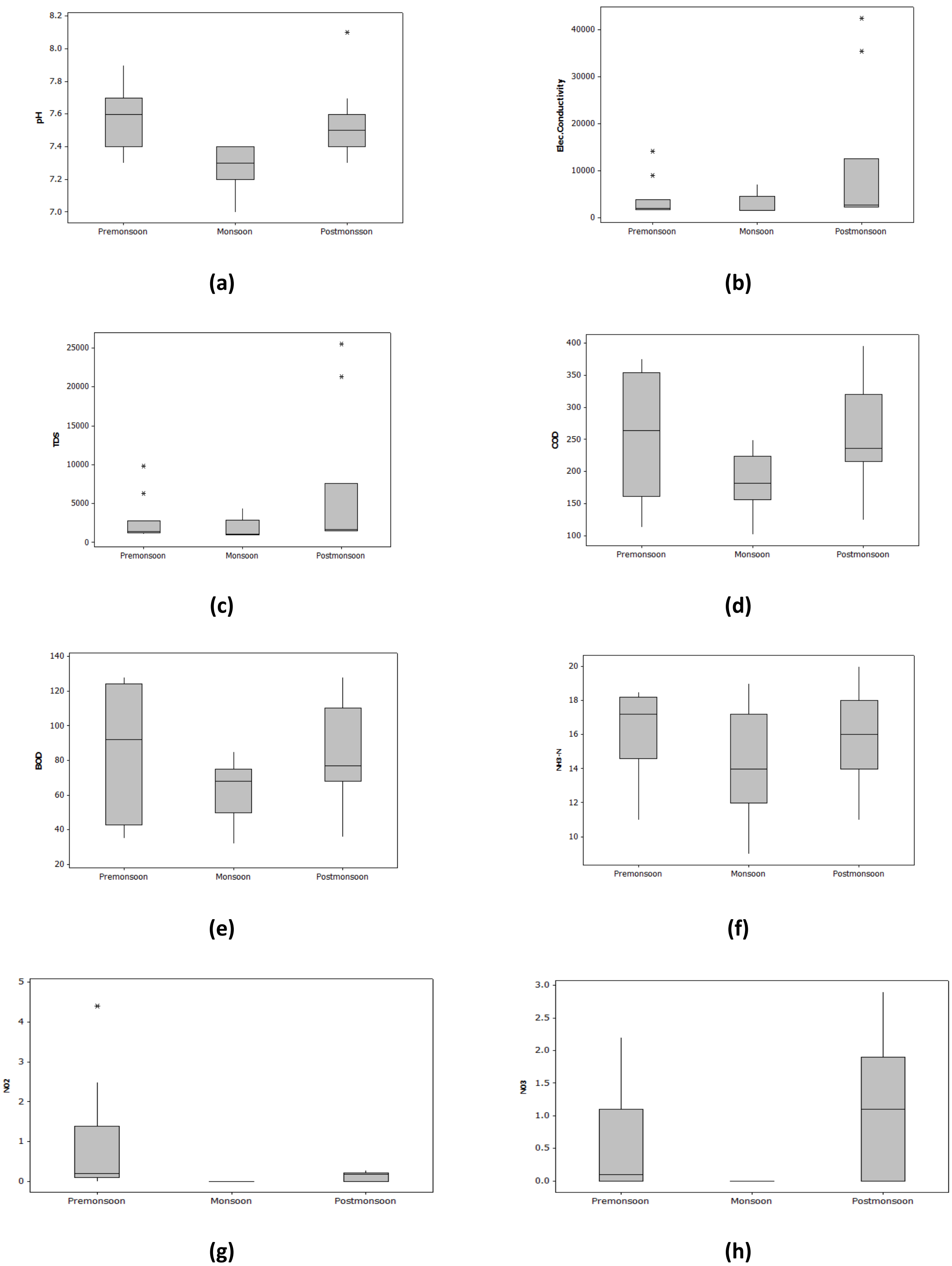


Figure 3. Box Whisker plot for (a) pH, (b) EC, (c) TDS, (d) COD, (e) BOD, (f) NH_3-N, (g) NO_2^- and (h) NO_3^-

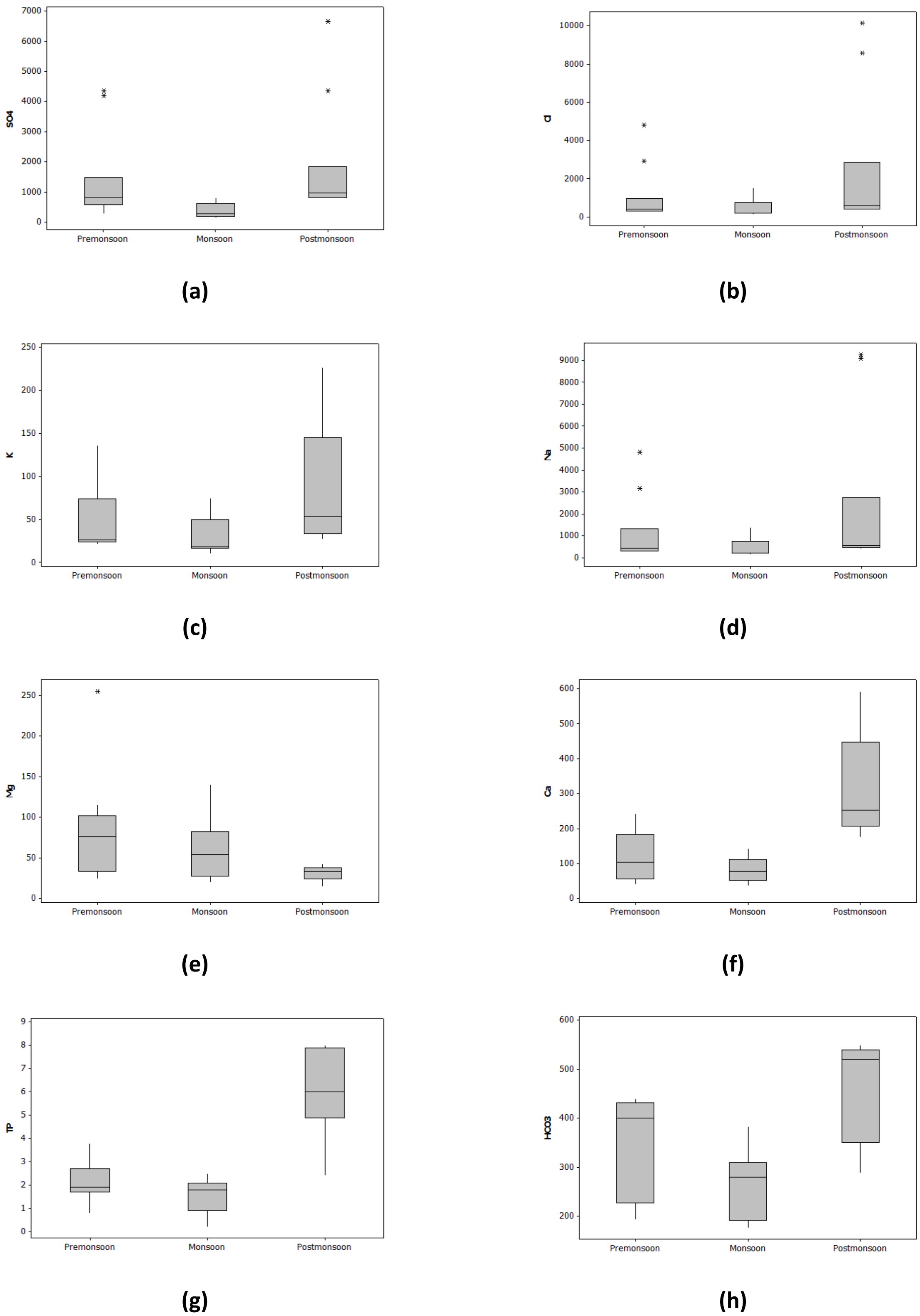


Figure 4. Box Whisker plot for (a) SO_4^{2-}, (b) Cl^-, (c) K^+, (d) Na^+, (e) Mg^{2+}, (f) Ca^{2+}, (g) TP and (h) HCO_3^-

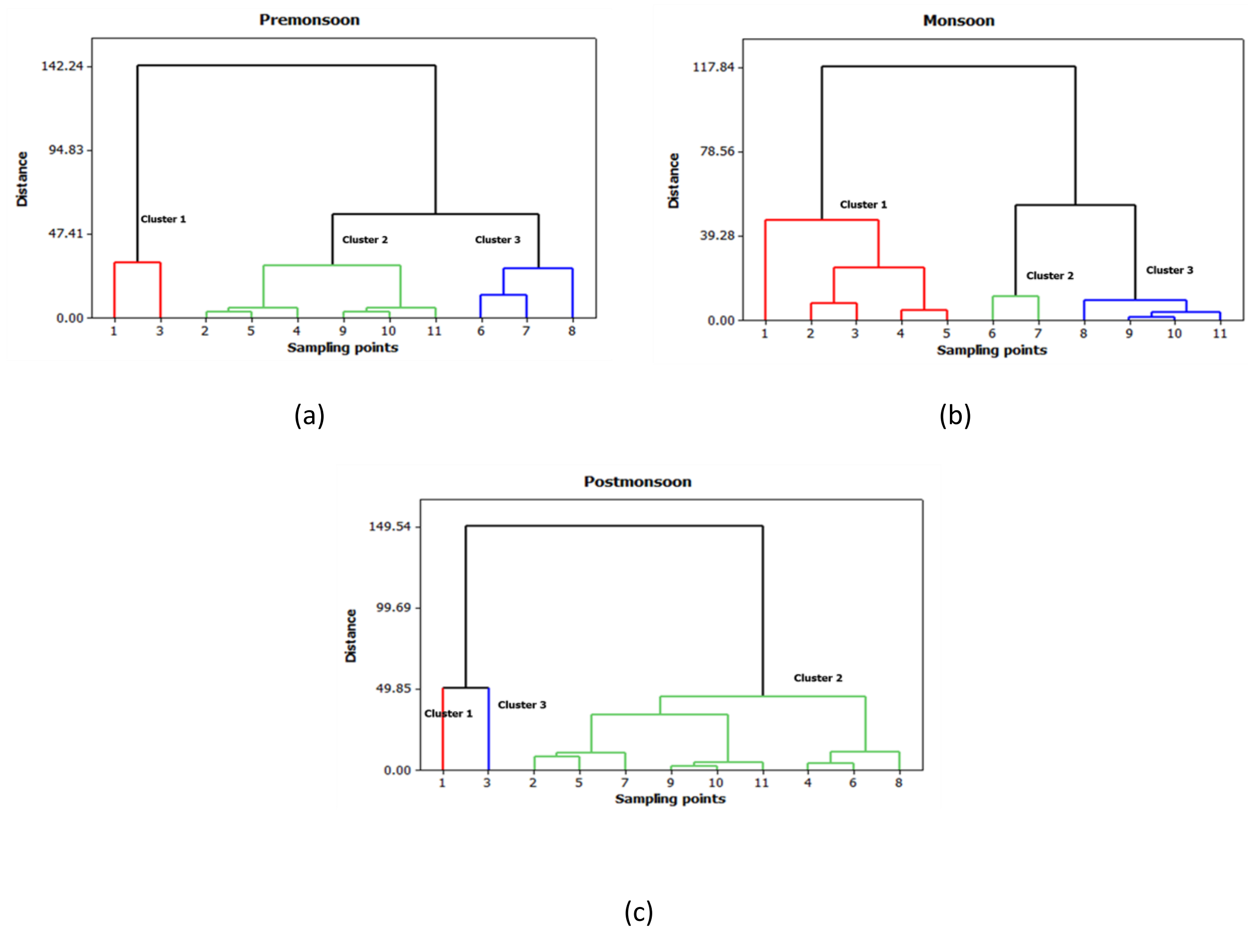


Figure 5. Dendrogram for (a) pre-monsoon, (b) monsoon and (c) post-monsoon

For all seasons, principle components with eigen values >1.0 that contributed to total variance were extracted from data set. For pre-monsoon and monsoon five components and for post-monsoon three components were extracted and are shown in Table 6 respectively. Liu *et al.,* (2003) classifies factor loading as strong, moderate and weak based on the absolute loading values >0.75; 0.75-0.5; 0.5-0.3 respectively. EC, TDS, SO_4, Cl, K, Na significantly contributed for PC1 with exhibiting variance of 48.1, 54.5 and 52.8 for all the three seasons. Similarly, COD and BOD significantly contributed for PC2 & PC3 with variance of 22%, 22.3% and 11.9% for all the three seasons. The former may be due to association of these components with natural influences on the ionic composition because of weathering and possible contribution of seawater, whereas, the later may be due to the significance of sewage/effluent loads in river. From Fig. 6, the loading plot for the principle component (PC1 & PC2) shows the seasonal distribution of the parameters. It can be noted that from the three seasons that the variables are noticeably distinguish between geogenic sources from the anthropogenic ones. Grouping of parameters (SO_4, TDS, Na^+, Cl^-, Ca^{2+}, EC, Mg^{2+}) in all the seasons suggest that they are correlated mutually. It also portrays the characteristic of samples that helps in understanding spatial distribution among them. Similarly, the score plot (Fig. 7) developed using PC1 & PC2 substantiate the clustering of samples from the specific site spatial distribution and their space.

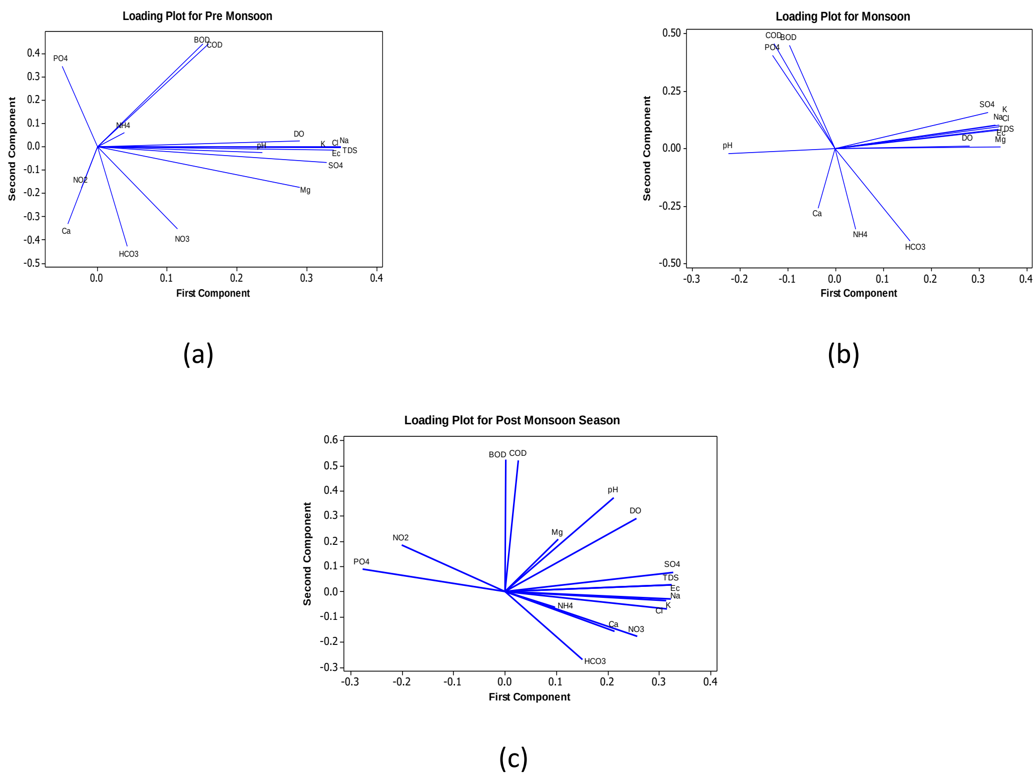


Figure 6. Loading plot for (a) pre-monsoon, (b) monsoon and (c) post-monsoon

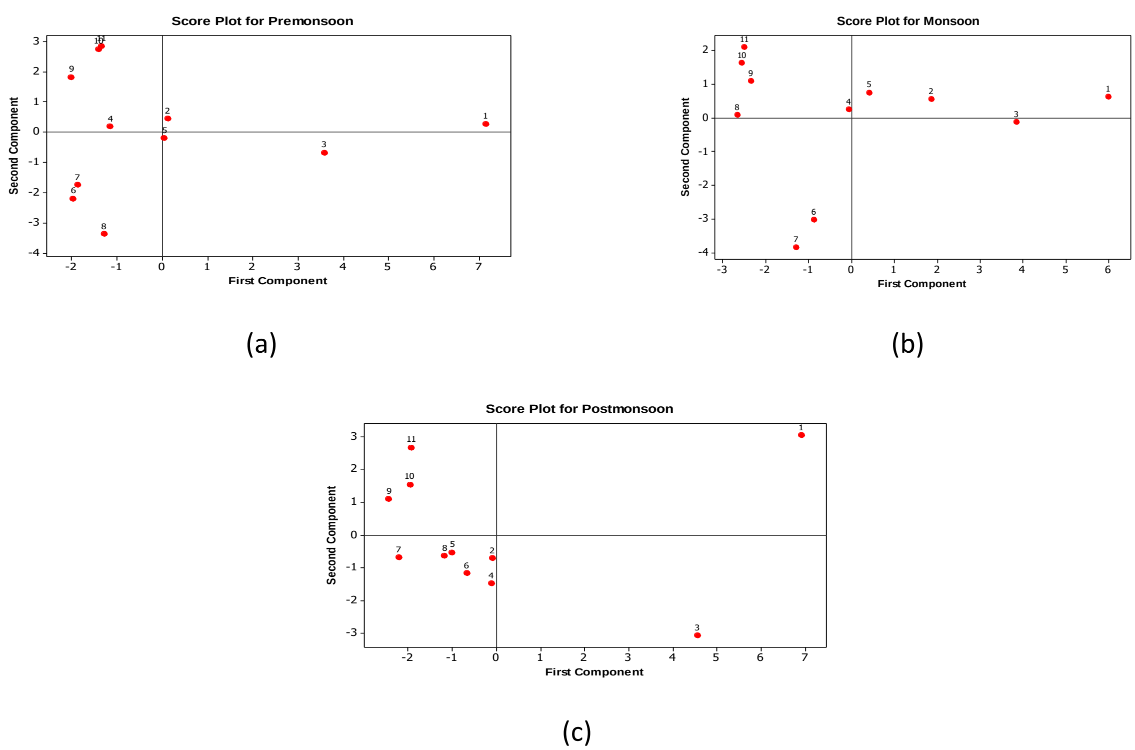


Figure 7. Score plot for (a) pre-monsoon, (b) monsoon and (c) post-monsoon

Table 9. Principal components matrix

Variable	Premonsoon					Monsoon				Post monsoon		
	PC1	PC2	PC3	PC4	PC5	PC1	PC2	PC3	PC4	PC1	PC2	PC3
pH	0.236	-0.025	-0.402	-0.271	0.299	-0.224	-0.019	-0.295	0.591	0.212	0.374	0.154
Ec	0.348	0.000	0.020	-0.001	-0.055	0.341	0.086	-0.031	0.070	0.323	0.025	0.156
TDS	0.349	-0.006	0.024	0.003	-0.042	0.343	0.084	0.039	0.055	0.323	0.025	0.156
DO	0.290	0.023	0.091	0.346	-0.332	0.281	0.014	0.287	0.139	0.256	0.291	-0.071
COD	0.151	0.448	-0.129	-0.027	-0.044	-0.129	0.458	0.178	0.184	0.026	0.520	-0.109
BOD	0.159	0.441	-0.103	-0.065	-0.011	-0.097	0.452	-0.096	0.394	0.001	0.523	-0.094
NH_3-N	0.038	0.060	0.655	0.190	0.181	0.042	-0.347	-0.504	0.033	0.097	-0.061	-0.529
SO_4^{2-}	0.328	-0.067	0.032	-0.181	0.071	0.318	0.158	-0.196	0.026	0.327	0.077	0.030
Cl^-	0.348	-0.003	0.043	-0.016	-0.047	0.343	0.098	0.051	0.030	0.315	-0.068	0.157
K^+	0.338	-0.015	0.035	-0.039	0.203	0.335	0.106	-0.074	0.130	0.314	-0.037	0.154
Na^+	0.348	-0.002	0.039	-0.006	0.022	0.342	0.104	-0.021	0.056	0.322	-0.031	0.142
Ca^{2+}	-0.043	-0.332	-0.155	0.142	-0.582	-0.036	-0.258	0.554	0.508	0.213	-0.158	-0.335
Mg^{2+}	0.290	-0.177	0.176	0.168	-0.206	0.346	0.008	0.011	-0.029	0.103	0.208	-0.475
HCO_3^-	0.042	-0.428	0.061	-0.017	0.354	0.155	-0.400	-0.253	0.391	0.151	-0.268	0.003
NO_2^-	-0.023	-0.177	-0.177	-0.606	-0.097	N.A	N.A	N.A	N.A	-0.201	0.185	0.451
NO_3^-	0.115	-0.353	-0.355	-0.339	-0.213	N.A	N.A	N.A	N.A	0.257	-0.178	-0.085
PO_4^{3-}	-0.051	0.348	0.346	-0.448	-0.388	-0.131	0.408	-0.341	0.022	-0.278	0.087	-0.064
Eigenvalue	8.180	3.900	1.819	1.206	1.074	8.176	3.345	1.406	1.002	8.971	3.452	2.028
Var.(%)	48.1	22	11.2	7.1	6.3	54.5	22.3	9.4	6.7	52.8	20.3	11.9
Cum. (%)	78.1	73	84.1	91.3	95.2	54.5	76.8	86.2	92.9	52.8	73.1	85

4. Conclusions

The physicochemical parameters of surface water samples collected from *Cooum* river have been assessed. The results reveal that river is polluted and cannot be used for domestic, irrigation & aquaculture purposes. Furthermore, the dissolved oxygen(DO) concentration is found near to Napier bridge (SW1) only and was completely absent in other sampling points, which clearly indicates that constraint of backwater flow to other sampling points due to accumulation of sediments in the *Cooum* river. Correlation studies indicated that strong positive correlation between major ionic concentration and organic loads with R^2>0.7. The majority ionic concentrations such as $Na^{2+,}$ Ca^{2+},Mg^{2+},Cl^- were higher at Napier bridge (SW1) clear indicating the positive response of backwater intrusion from sea and limited to that level which can enhance the development of mangrove vegetation and aquatic organisms. The grouping by HCA for sampling stations and the principle component analysis revealed that influence of anthropogenic activities is the main source of pollution in the river. Hence, it is imperative that it is necessary to maintain minimum flow requirement to keep the water in good condition and continuous monitoring is essential to assess the impact of pollution loads in the *Cooum* river.

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