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Research Article

Assessment of Seasonal Disparity on Hydrogeochemical Facies Distribution in Cooum River, India

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Abstract

Objective: The environmental stress such as climatic conditions, anthropogenic activities on river water quality and its flow is of challenging interest. In the present study, evaluation of the surface water (in Cooum river, India) quality and the seasonal impact have been investigated. **Methodology:** Hydrogeochemical facies such as piper plots, chloroalkali indices, Kelly index, sodium absorption ratio, magnesium hazard and rock water interaction have been considered to understand the ionic constituents, geochemistry of the river water and its influence on water quality. The water samples were collected seasonally during March, 2013-2014 and are categorized as pre-monsoon, monsoon and post-monsoon. **Results:** The investigation results reveal that the ionic concentration and organic loads exhibit for all three seasons indicating the anthropogenic activities. **Conclusion:** The rock water interaction shows that plagioclase weathering is mainly dominant in the sampling sites and the ionic constituents were due to seawater intrusion and gypsum dissolution in the water.

Key words: Hydrogeochemical facies, SAR, chloroalkali indices, rock water interaction, piper plot

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Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

River is the key in maintaining the ecological setting, such as flora and fauna of the ecosystem¹. Rivers are considered too vulnerable water bodies as they tend to carry the wastewater from drainage basins². The various factors such as rainfall, temperature, rock water interactions and other activities plays crucial part of river water quality and the seasonal variation of these factors has a significant role in concentration of pollutants in the river water. Also, the seasonal variation act as a very important factor in controlling the water cycle with active agents of transport such as ions and minerals etc.¹. These agents may be in the form of suspended or in dissolved, from the source and has ability to deposit at different locations based on their physicochemical nature³. Hence, it is vital to monitor and prevent river pollution and to have dependable information on the quality of water for effective management². Ionic constituents present in the river water is relatively small, but significant amounts and are usually originate from weathering of rocks, soil, dissolution of lime, gypsum and other soil minerals⁴. The variation in river water quality based on the hydrological factors and geochemical variations have been investigated and reported by researchers Shrestha and Kazama⁵, Hellar-Kihampa *et al.*⁶, Koklu *et al.*⁷, Kumarasamy *et al.*³ and Singh *et al.*².

Overall literature study suggests that rock weathering and erosion are the two major factors that attribute to the changes in the geochemistry of elements on earth and also the cause for the transport of dissolved and particulate materials by rivers to the sea. Krishnaswami and Singh⁸ suggested characterising river water with respect to dissolved and particulate concentration of various ions and components in order to understand the rock weathering process. In addition, the rapid urbanization along the river basin is very crucial of the vulnerability of river water quality due to anthropogenic pressures^{9,10}. Hydrogeochemical facies are the best indicators to study about the geochemical interactions in the subsurface of river. Tools such as piper plots, sodium hazard ratio and magnesium hazard helps to identify the influence of ionic constituents and their impact on the river water quality. Cooum river flowing inside the city has been polluted heavily due to anthropogenic activities. Understanding the river quality is very important, as the geology and the river water characteristics depends on the factors such as interaction with solid phases, residence time and anthropogenic impacts¹¹. Hence, in this study the seasonal variation on the hydrogeochemical facies, rock water interactions of Cooum river flowing inside the Chennai city have been investigated.

MATERIALS AND METHODS

Study area: River Cooum originates from Kesavaram dam and 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. 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. The river can be divided into two streams namely upstream and downstream, which is based upon the stretch of the river. The upstream is the flow of river flowing till urban area (Chennai city) and downstream stream is the river flowing inside the urban area (Chennai city). In this study, 11 locations (Fig. 1) have been identified to collect samples from the 18 km stretch of river basin in Chennai city. The study area along with the sampling points is shown in the Fig. 1.

Methodology: The surface water samples from Cooum river were collected from 11 different sampling points in an 18 km stretch of river, which passes through Chennai city. All the samples were collected in pre-sterilized polyethylene bottles and utmost care was taken to fill the bottles without air bubbles at each sampling site during March, 2013-2014 and categorized as pre-monsoon, monsoon and post-monsoon. The sampling locations and their designation are shown in Table 1. The collected samples were labelled and taken into the laboratory using a refrigerator box. The parameters such as pH and Electrical Conductivity (EC) were measured using potable kit (ELICO, India) at the site during sampling. The analysis of water quality parameters such as pH, Electrical Conductivity (EC), Total Dissolved Solids (TDS), Dissolved Oxygen (DO), sulphate (SO₄), chloride (Cl), potassium (K), sodium (Na), calcium (Ca), magnesium (Mg), carbonate (CO₃²⁻) and bicarbonate (HCO₃⁻) have been analysed by following the standard procedure prescribed by American Public Health Association¹². The sampling points in the Cooum river stretch were Napier bridge (SW1), Flag house (SW2), New Secretariat (SW3), Jail Cemetery (SW4), Chindadripet bridge (SW5), Chitratalkies bridge (SW6) and Erson bridge (SW7), Namasivayapuram causeway (SW8), Annanagar bridge (SW9), Aminjikarai bridge (SW10) and Koyembedu bridge (SW11). The analytical data quality was ensured through standardization experiments with duplicates and average has been reported. Statistical analysis for the data such as piper plot and rock water interaction was performed using Aquachem software in order to identify the insights of distribution of composition of Cooum river.

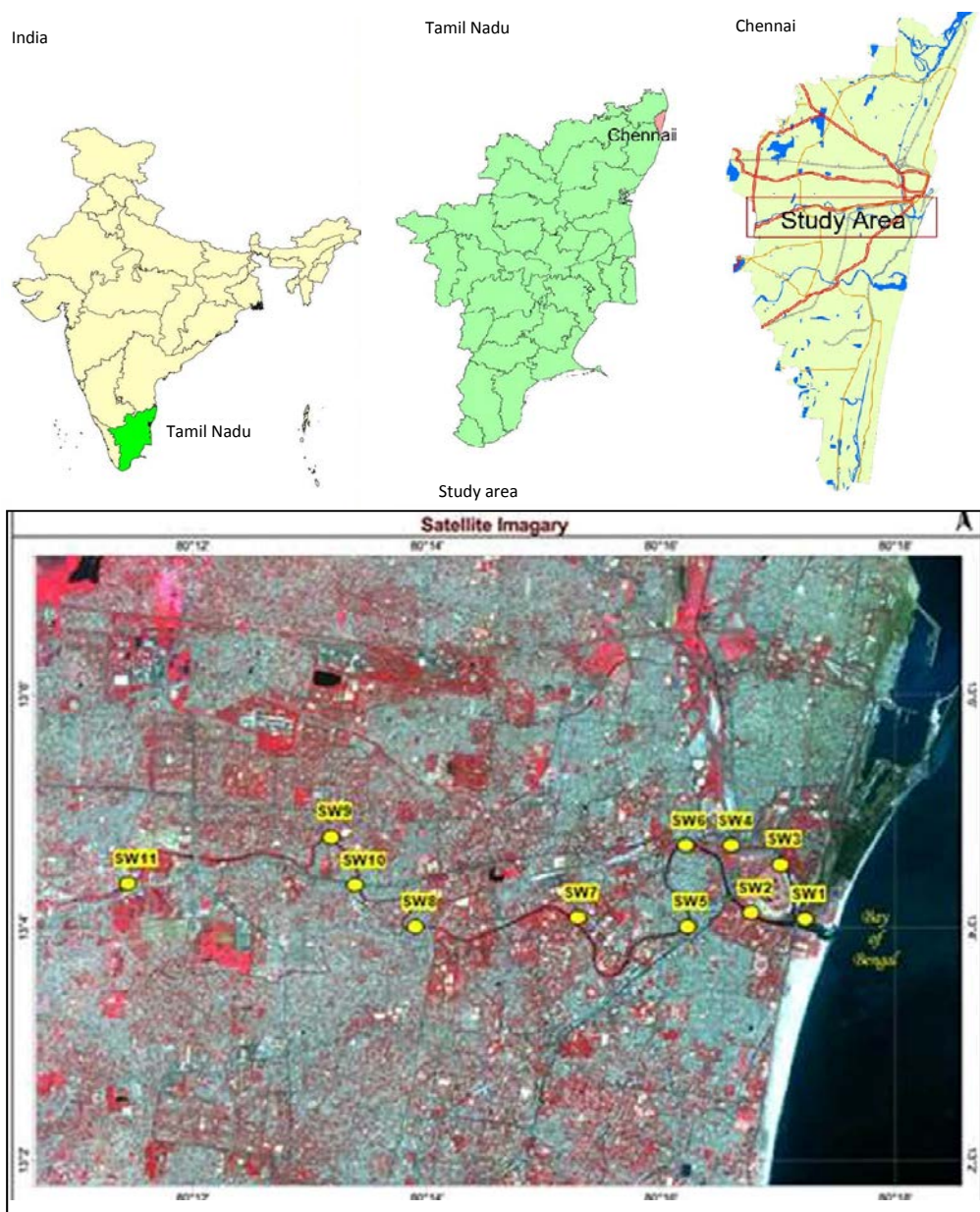


Fig. 1: Sampling locations in the downstream of Cooum river, source of image IRS P6 LISS III, national remote sensing centre, Hyderabad. Month and year of image March, 2013

RESULTS AND DISCUSSION

Hydrogeochemical facies: The physicochemical parameters of the Cooum river has been presented in Table 1. The hydrochemical analysis plot was made using trilinear piper plot¹³ which is based on the domination of ions. The piper plots of the seasonal variation of Cooum river are presented in Fig. 2. The classification of cation and anion facies, in terms of major ion percentage and water types is based on the

domain, in which they occur on the fragments of diagram^{14,15}. It can be noted from the figure that during pre-monsoon season (Fig. 2a), 10 sampling points falls in Na-Cl type and only one sampling point falls in mixed Ca-Mg-Cl. From data plots of hydrogeochemistry it is easily noted that 8 sampling points have dominated Na and K and 3 sampling points shows no dominant type. For ionic constituents, 8 sampling points showed anionic faces (SO₄,Cl) and 3 were no dominant type. During monsoon season (Fig. 2b), 9 samples of the study

Table 1: Physicochemical characteristics of Cooum river

Physicochemical characteristics											
Sampling points	pH	EC	TDS	SO ₄	Cl	K	Na	Ca	Mg	CO ₃	HCO ₃
Pre-monsoon											
SW1	7.7	14160	9820	4210	4829	136	4803	132	255	0	340
SW2	7.6	3925	2775	1470	973	74	1331	56.1	76	0	430
SW3	7.9	9100	6270	4360	2920	106	3173	104	98	0	400
SW4	7.5	2034	1456	710	587	47	678	40	68	0	390
SW5	7.6	3876	2740	1020	933	57	1107	48	102	0	440
SW6	7.3	1806	1230	864	316	24	296	184	116	0	424
SW7	7.4	1810	1240	820	312	25	358	220	76	0	432
SW8	7.7	2028	1380	650	356	26	310	244	84	0	440
SW9	7.4	1696	1103	280	308	21.3	305	80	27	0	200
SW10	7.6	1846	1119	320	328	23	312	88	24	0	194
SW11	7.5	2520	1644	570	422	24.4	432	124	34	0	228
Monsoon											
SW1	7	7140	4385	815	1529	75	1402	112	140	0	306
SW2	7.2	4580	2852	630	772	50	760	36	82	0	240
SW3	7.2	6720	3842	785	1138	70	1173	85	99	0	310
SW4	7.4	3486	2024	453	440	38	540	52	58	0	340
SW5	7.3	3520	2290	635	584	41	641	42	64	0	280
SW6	7.1	1642	1030	154	212	10	208	88	54	0	294
SW7	7.4	1650	1052	185	140	18	158	140	32	0	384
SW8	7.4	1550	924	140	156	17	180	144	28	0	240
SW9	7.2	1510	920	190	200	17	210	77	22	0	192
SW10	7.3	1650	972	280	190	14	212	72	20	0	176
SW11	7.3	1686	1022	270	200	17	212	78	28	0	188
Post-monsoon											
SW1	8.1	42400	25520	6660	8589	227	9110	472	43	0	549.00
SW2	7.6	12600	7580	1850	2854	145	2740	368	24	0	539.24
SW3	7.5	35500	21360	4360	10147	207	9250	448	29	0	500.20
SW4	7.4	2780	1692	1710	1289	43	1155	593	38	0	463.60
SW5	7.5	7320	4460	1020	1425	55	1315	248	24	0	531.92
SW6	7.3	2330	1420	864	460	54	466	424	34	0	539.24
SW7	7.5	2360	1490	820	480	34	520	176	15	0	519.72
SW8	7.4	2260	1380	780	410	57	405	208	43	0	536.80
SW9	7.5	2600	1592	885	430	27	405	216	34	0	312.32
SW10	7.5	2700	1642	790	420	31	455	193	32	0	351.36
SW11	7.7	3320	2012	970	600	36	575	254	37	0	287.92

area fall in Na-Cl and 2 samples falls in mixed Ca-Mg-Cl. Further, from data plots, it can be noted that hydro geochemistry of 9 sampling points is dominated with Na and K and 2 sampling points exhibits no dominant type. Likewise, 3 sampling points were dominated in chloride type and 8 sampling points shows no dominant type. Similarly, during post-monsoon season (Fig. 2c), it can be noted from the figure that all 11 samples falls in Na-Cl. From data plots, hydrogeochemistry is dominated by 10 sampling points that possess Na and K and 3 exhibits no dominant type. For ionic constituents, 5 sampling points exhibits chloride type, 4 sampling points showed no dominant type and 2 sampling points possess SO₄ type. It is evident from the plots that Na⁺-Cl⁻ and Ca⁺-Na⁺-HCO₃⁻ are the two major types present in study area, which is agreed with results of dominant and cations.

The indices such as of chloroalkaline indices (CAI and CAII), Sodium Absorption Ratio (SAR), Kelly's Index (KI) and

Magnesium Hazard (MH) for the surface water were calculated and are presented in Table 2. In order to observe changes in the chemical constituents during surface water runoff¹⁶, the calculation of chloroalkaline indices (CAI and CAII) helps to give an indication of ion exchange between the subsurface water and its environment¹⁷⁻¹⁹. The chloroalkali indices indicates the ion exchange process i.e., Ca²⁺ and Mg²⁺ from the surface water will be exchanged between Na⁺ and K⁺ of the host rock. Both the indices CAI and CAII can yield positive and negative values based upon the nature of the water. Negative value indicates the process of normal ion exchange process and positive value indicates the reverse exchange process in the surface water. In the present study, the chloroalkali indices exhibits positive values of surface water analysed indicating the reverse exchange process in the study area.

Kelly's index and magnesium hazard were calculated for the surface water for all the three seasons. Kelly's index

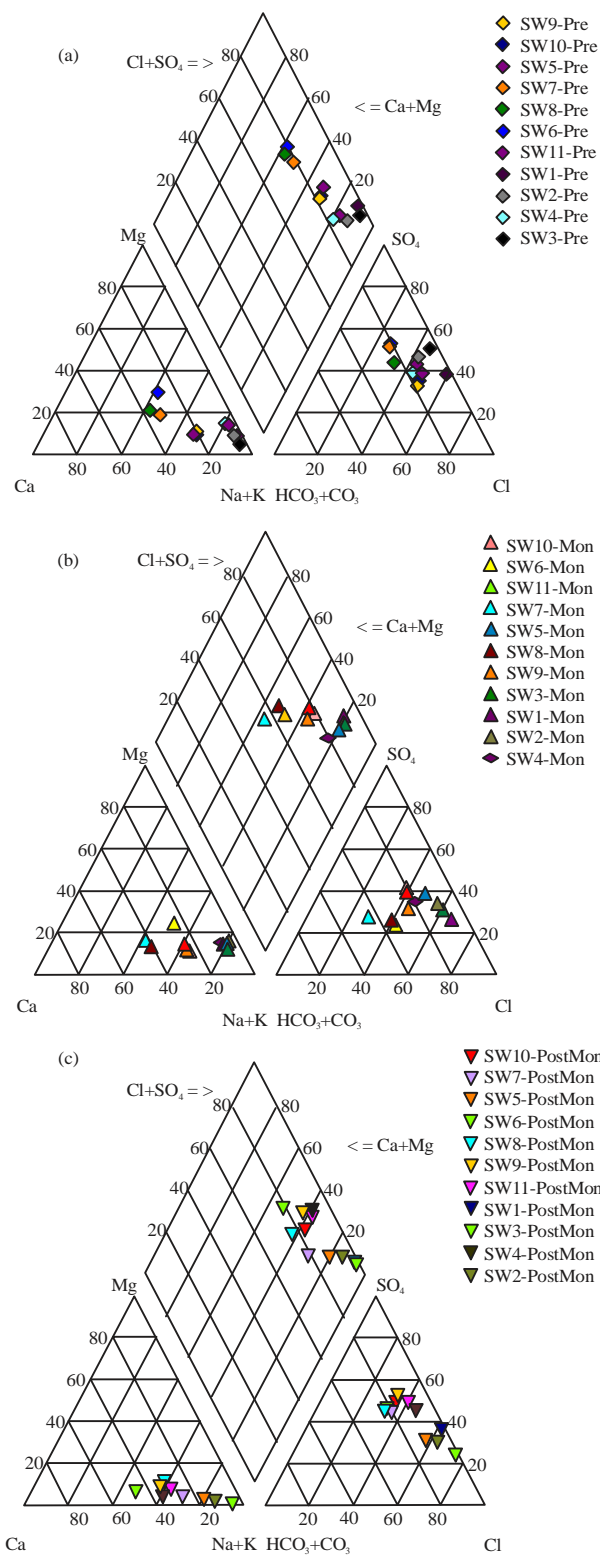


Fig. 2(a-c): Piper trilinear plots of seasonal variation in Coom river (a) Pre-monsoon, (b) Monsoon and (c) Post-monsoon

of more than one indicates that water is unfit for any agricultural/domestic purposes. It can be noted from Table 1

that all the sampling locations falls over unity for all the three seasons indicating unsuitability of water for any other practical

Table 2: Hydrogeochemical facies distribution over Cooum river

Seasonal variation	Sampling points	Parameters				
		CAI	CAII	SAR	KI	MH
Pre-monsoon	SW1	4827.97	340.97	345.280	12.41	65.89
	SW2	971.55	429.70	163.770	10.07	57.53
	SW3	2918.87	401.31	315.720	15.70	48.51
	SW4	585.76	389.80	92.264	6.27	62.96
	SW5	931.75	440.77	127.820	7.38	68.00
	SW6	314.98	425.09	24.160	0.98	38.66
	SW7	310.77	431.91	29.420	1.20	25.67
	SW8	355.05	442.23	24.200	0.94	25.60
	SW9	306.94	199.93	41.690	2.85	25.23
	SW10	326.97	193.97	41.690	2.78	21.42
	SW11	420.91	228.03	48.600	2.73	21.51
Monsoon	SW1	1528.03	306.06	124.900	5.56	55.55
	SW2	770.95	239.93	98.940	6.44	69.49
	SW3	1136.90	309.86	122.290	6.37	53.80
	SW4	438.68	339.69	72.810	4.90	52.72
	SW5	582.83	279.84	88.040	6.04	60.37
	SW6	210.97	293.96	24.680	1.46	38.02
	SW7	138.74	383.80	17.030	0.91	18.60
	SW8	154.73	239.70	19.400	1.04	16.27
	SW9	198.86	191.85	29.840	2.12	22.22
	SW10	188.81	175.87	31.250	2.30	21.73
	SW11	198.85	187.89	29.120	2.00	26.41
Post-monsoon	SW1	8587.91	551.38	567.710	17.68	8.34
	SW2	2852.98	539.22	195.710	6.98	6.12
	SW3	10146.07	503.25	598.950	19.39	6.07
	SW4	1288.07	465.05	65.020	1.83	6.02
	SW5	1424.03	533.75	112.760	4.83	8.82
	SW6	458.86	540.27	30.790	1.01	7.42
	SW7	478.84	519.62	53.210	2.72	7.85
	SW8	408.87	538.63	36.15	1.61	17.13
	SW9	428.99	312.31	36.22	1.62	13.60
	SW10	418.84	351.27	42.89	2.02	14.22
	SW11	598.98	287.90	47.66	1.97	12.71

purposes. Similarly, magnesium hazard (high levels of magnesium) will degrade the soil quality by converting to alkaline and make it unsuitable for any plantation near the banks of the river.

Salinity and sodium hazard: Sodium Absorption Ratio (SAR) is used to predict the sodium of high carbonate water in the absence of no residual alkali⁴. It is also the measure of relative proportions of sodium ions in aqueous phase to those of calcium and magnesium²⁰ and can be calculated by using the Eq. 1:

$$SAR = \frac{Na^+}{\sqrt{(Ca^{2+} + Mg^{2+})/2}} \quad (1)$$

For the present study, based on the USSS diagram, the hazard nature was found out by correlating SAR and EC and are shown in the Fig. 3. It can be noted from the figure

that during pre-monsoon, sampling points (S1-S5) exhibits high levels of sodium hazard and sampling points (S6-S11) exhibits medium and low levels of sodium hazard. Similarly, during monsoon season, sampling points (S1-S4) falls in high levels and points (S5-S11) exhibits moderate and lower level of sodium hazard. However, the ratio is less than pre-monsoon level indicating the impact of rainfall among the sampling points. While, post-monsoon analysis exhibited sampling points (S1-S5, S7 and S11) indicating high levels of sodium hazard and points (S6, S8-S10) shows low level of sodium hazard indicating high levels of pollutant discharge through anthropogenic activities.

Salinity hazard was high during post-monsoon season when compared with pre-monsoon and monsoon season. During pre-monsoon season sampling points (S1-S5) exhibits C4, which is very high level of salinity hazard which may be due to the intrusion of ocean water and sampling sites

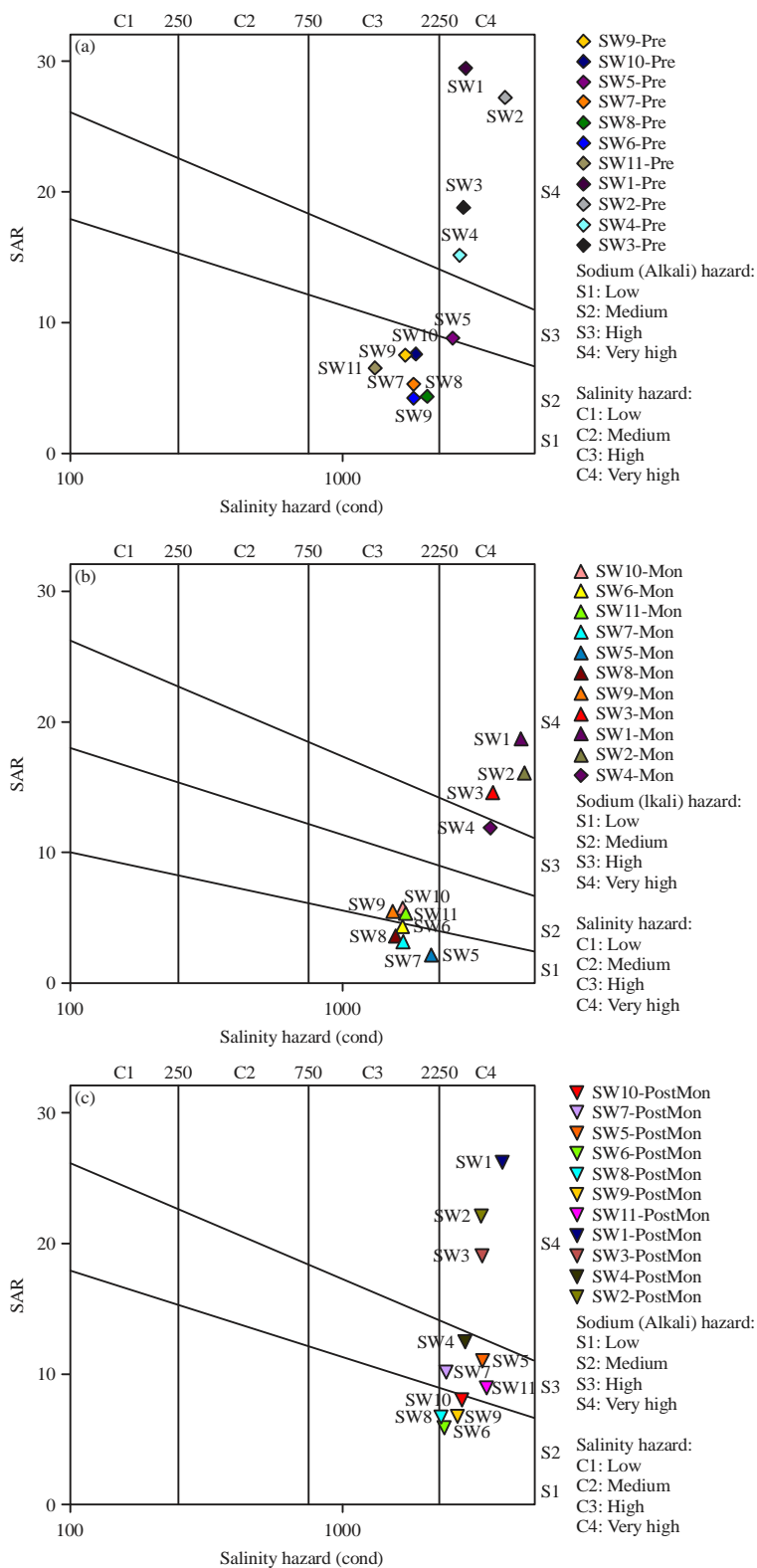


Fig. 3(a-c): SAR vs salinity hazard for river Cooum during various season (a) Pre-monsoon, (b) Monsoon and (c) Post-monsoon

(S6-S11) shows low level of salinity hazard. Similarly, sampling sites (S1-S4) reveals the presence of high level of salinity hazard and other sites (S5-S11) exhibited low salinity hazard indicating effect of the rainfall over the season.

Table 3: Effect of seasonal variation of rock water interaction over Cooum river

Parameters	Range values	Conclusion	Range (No. of samples)					
			Pre-monsoon	Percentage	Monsoon	Percentage	Post-monsoon	Percentage
(Na+K-Cl)/ (Na+K-Cl+Ca)	>0.2 and <0.8	Plagioklase weathering possible	0.873-0.922 (05)	45.4	0.307-0.776 (07)	63.6	0.873-0.922 (05)	54.5
	<0.2 or >0.8	Plagioklase weathering unlikely	0.237-0.552 (06)	54.5	0.818-0.853 (04)	36.3	0.237-0.552 (06)	54.5
Na/(Na+Cl)	>0.5	Sodium Source other than halite-albite	0.573-0.678 (11)	100	0.586-0.654 (11)	100	0.587-0.626 (11)	100
	= 0.5	Ion exchange	-	-	-	-	-	-
	<0.5, TDS>500	Halite solution	-	-	-	-	-	-
	<0.5, TDS<500 and >50	Reverse softening, seawater	-	-	-	-	-	-
Ca/(Ca+SO ₄)	= 0.5	Gypsum dissolution	0.473 (01)	9.09	0.493 (01)	9.09	0.145-0.390 (09)	81.8
	<0.5 and pH<5.5	Pyrite oxidation	-	-	-	-	-	-
	<0.5 and pH neutral	Calcium removal-ion exchange or calcite precipitation	0.054-0.406 (10)	90.9	0.120-0.409 (07)	63.6	0.454-0.540 (02)	18.1
	>0.5	Calcium source other than gypsum-carbonate or silicates	-	-	0.578-0.711 (03)	27.2	-	-
TDS	>500	Carbonate weathering or brine or seawater	1103-9820 (11)	100	920-4385 (11)	100	1380-25520 (11)	100
	<500	Silicate weathering	-	-	-	-	-	-
Cl/Sum anions	>0.8 and TDS>500	Seawater or brine or evaporites	-	-	-	-	-	-
	>0.8 and TDS<100	Rainwater	-	-	-	-	-	-
	<0.8	Rock weathering	0.357-0.734 (11)	100	0.449-0.762 (11)	100	0.406-0.842 (11)	100
HCO ₃ /Sum anions	>0.8	Silicate or carbonate weathering	-	-	-	-	-	-
	>0.8 and SO ₄ >20 meq L ⁻¹	Gypsum dissolution	0.03-0.163 (4)	36.3	-	-	0.024-0.149 (6)	54.5
	<0.8 and sulfate low	Seawater or brine	0.173-0.30 (7)	63.6	0.089-0.409 (11)	100	0.193-0.308 (5)	45.4

Rock source deduction: Rock source deduction helps to gain insight to the possible origin of water samples. These results presents a general overview based on the ion ratio found in a sample, which are compared to the ratios of respective ions in reactive minerals. Table 3 provides the summary of criterion of rock source deduction²¹. It can be noted from the Table 3 that Plagioklase weathering was dominant during monsoon season indicating 63% of sampling points were recorded. The sodium ion was predominant over all the sampling points, which may be due to sodium source other than halite-albite as shown in the Table 3. The presence of calcium ions were high exhibiting 90% of sampling points during pre-monsoon season followed by 63% of sampling points during monsoon season, which is due to ion exchange or calcite precipitation. The total dissolved solids in the samples were due to carbonate weathering or brine or seawater intrusion in all the sampling points. Similarly, the chloride ratio in all sampling points showed that influence of rock weathering of the Cooum river. During pre-monsoon and post-monsoon the presence of HCO₃ was 36 and 54% indicating gypsum dissolution due to natural process in the sampling points. However, during monsoon season all the points exhibited

higher level of HCO₃, which is due to mixing of sea water and dissolution of atmospheric CO₂ in other areas.

CONCLUSION

This study reports the influence of seasonal variation on hydro geochemistry of surface water of Cooum river basin. It was noted that the Plagioklase weathering was very high particularly in monsoon season. In addition, it is also noted calcium precipitation, carbonate weathering and rock weathering is also predominant characteristics found in the Cooum river. The presence of Na⁺-Cl⁻ and Ca⁺-Na⁺-HCO₃⁻ ionic types were found to be more dominant in the study area of Cooum river stretch. Similarly, the analysis of the hydrogeochemical indices such CAI, CAIL, SAR, KI and MH indicated that all the sampling points of the Cooum river exceeds the permissible limits for domestic use and water is not suitable for living of aquatic organisms in river water, which is mainly due to the anthropogenic activities. The results reveal that river is polluted and not suitable for domestic, irrigation and aquaculture purposes. Hence continuous monitoring and cleaning mechanism mainly

desilting of deposition of hazardous silt is essential to assess the impact of pollution loads and restoration of Cooum river.

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