RESEARCH ARTICLE

SEASONAL VARIATION OF WATER QUALITY PARAMETERS IN ENNORE ESTUARY WITH RESPECT TO INDUSTRIAL AND DOMESTIC SEWAGE

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ABSTRACT

A study has been undertaken to enlighten the influence of industrial and domestic sewage on the water quality parameters during postmonsoon, summer, premonsoon and monsoon in Ennore creek. The concentrations of the water quality parameters especially the nutrients were above the permissible limits of the coastal standards. Total alkalinity, pH and dissolved oxygen were below the coastal standards. The stations 3 and 4 at the Ennore creek had contributed the ubiquitous distribution of nutrients in the creek. The monsoon season experienced chaotic concentrations of nutrients. Along the creek concentrations of nutrients and other water quality parameters could have been controlled by the anthropogenic inputs from point and non-point sources.

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INTRODUCTION

Estuaries are complex and dynamic environmental components which receive large amounts of contaminants from urban and industrial sites (Leight *et al.,* 2005). Industrialization and urbanization of the coastal region often lead to decrease in coastal resource and destruction of natural defence structures (Zhao *et al.,* 2011). Agricultural, industrial and urban activities are considered to be major sources of addition of nutrients to aquatic ecosystems (Kucuksezgin *et al.,* 2006). Eutrophication is of great environmental distress, leading to diverse problems such as toxic algal blooms, loss of oxygen, fish mortalities and eventually loss of biodiversity (Yadav *et al.,* 2007). India has a long coastline of 8,129 km and of this 6,000 km is rich in estuaries, creeks, brackishwater, lagoons and lakes. The southeast coast of India is an important stretch of coastline, where many major rivers drain into the Bay of Bengal and they are also richer in marine fauna than the western coast of India. Chennai, the capital of Tamilnadu, India is located on the northern end of the Tamilnadu coast. Ennore is on the northeast coast of Chennai. (Venkatachalapathy *et al.,* 2010). Ennore coast consists of alluvial tracts and beach dunes, tidal flats and creek in the

eastern part. Ennore comprises of lagoons, with salt marshes and backwaters, which are submerged under water during high tide and form an arm of the sea opening in to the Bay of Bengal (Kannan *et al.,* 2007). Ennore creek was once encompassed with rich biodiversity and in due course of time has been totally wiped out by the petrochemical complex by pumping their effluents into the Ennore Creek. Consequently the natural wealth is eroded to mere sewage channel and the biological productivity of the coast has come down (Jayaprakash *et al.,* 2005).

Ennore coast receives untreated sewage from Royapuram sewage outfall, untreated / treated industrial effluents from Manali Industrial Belt, which houses many chemical industries. The dredging activities in Ennore area result in changes in the landscape, sediment transport, and dust pollution to the coast by quarrying process (Palanisamy *et al.,* 2006). Ennore estuary is connected with the Buckingham canal, which is polluted by urban sewage and industrial effluents and wastes generated by innumerable slum dwellers who live along its banks. So long as the assimilating capacity of the water body is not exceeded, the ecosystem is able to recover from additional stresses without permanent damage (Muthuraj and Jayaprakash, 2007).

Input of large quantities of nitrates and phosphates in to rivers causes eutrophication (Yang *et al*., 2010; Cuihong *et al.,* 2011). In extreme cases, excess nutrients loading in coastal regions result in the formation and proliferation of large scale opportunistic macroalgal blooms (Kuidong *et al.,* 2011). Problem of water resources are of three main types, namely too little water, too much water, and polluted water (Adebola, 2001). Aquatic pollution started long back but intensified during the last few decades, and now the situation has become alarming, especially in India (Bowen and Depledge, 2006; Girija *et al.,* 2007). Application of different multivariate statistical techniques help to identify important components accounting for most of the variances of a system in identifying temporal and spatial variation and sources of pollution in coastal water (Yidana *et al.,* 2008; Wu *et al.,* 2009).

MATERIALS AND METHODS

Study area description

Ennore creek (13°13'54.48" N, 80°19' 26.60" E) (Figure 1) is located in the northeast coast of metropolitan Chennai city, India. The total area of the creek is 2.25 sq km and is nearly 400 m wide. Its channels connect it to the Pulicat lake to the north and to the Kortalaiyar river in the south (Kannan *et al.,* 2007). Araniar and Kortalaiyar are the two seasonal rivers which transverse Ennore creek. They depend upon northeast monsoon during October to December.
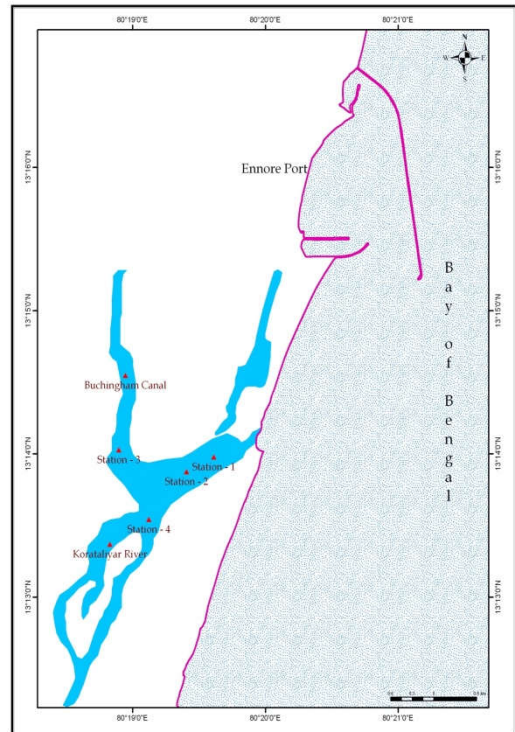
*Map was designed from ARCGIS 9.0

Fig. 1. Ennore creek

The flow of water in the rivers is not consistent and is scanty during most part of the year. The Kortalaiyar river drains into the back waters and ultimately reaches the sea through the Ennore creek. They confluence in brackish water bodies, mangroves situated at the fringes of Ennore creek

and Buckingham canal. It sustained a whole range of salt pans. Pollutants let out by industries, municipal and domestic sewage, tar, oil, chemical effluents and the filth of the city have mauled the once pristine Ennore creek. Industrial effluents and sewage gets concentrated because of the closure of the creek due to sand accretion caused by port construction. The chief threats to the coastal ecology and coastal communities are also in the form of North Chennai Thermal Power Station (NCTPS) and the petrochemical park along the coastal stretches from Ennore to Kattupalli village (Jayaprakash *et al.,* 2005).

Sample collection

In order to assess the impact generated by the anthropogenic activities in the Ennore creek, water samples were collected during the period of January-December 2008. The study period was divided into four seasonal groups: post-monsoon (January, February and March), summer (April, May and June), pre-monsoon (July, August and September), monsoon (October, November and December). In Ennore estuary, four sampling locations were selected: Station I- the bar mouth region (13°14'02.31" N, 80°19'49.47" E), Station II- creek (13°13'52.54" N, 80°19' 24.26" E), Station III- the Buckingham canal (north towards Pulicat lake) (13°14'02.72" N, 80°18' 54.18" E) and station IV- right down the railway bridge (13°13'30.39" N, 80°19' 02.30" E).

Sample Processing

Samples for water quality analysis were collected using 1 L Polyethylene-Tereftalate (PET) bottles. The samples were kept at 4°C in icebox, transferred to the laboratory and stored at -20°C until analysis in deep freezer. The samples for the water quality was not acidified due to the reason that the nitrate analysis runs in cadmium reduction column, passing acid contained sample will deactivate the column, therefore the samples were stored at 4°C in icebox following internationally recommended protocols (APHA, 1998). The glassware's for nutrient analysis were washed with Extran -04 (Phosphate-free- Merck) soap solution followed by acid wash and washed with distilled water.

Water quality analysis

Temperature and pH

Temperature (°C) was measured using mercury filled Celsius thermometer with an accuracy of 1°C. pH was measured using digital pH meter with glass calomel electrode, pH 0.01 accuracy.

Salinity and Dissolved oxygen

Salinity (PSU) was determined by Mohr-Knudsen argentometric titration method, using standard solution of silver nitrate (Merck) to precipitate halide ions in seawater using potassium chromate (Merck) as an indicator to form silver halides, presence of excess silver ions lead to the formation of red silver chromate (the endpoint of titration). Dissolved oxygen (mg/l) was determined in seawater by Winkler's method, dissolved oxygen in water reacted with manganese hydroxide in strongly alkaline medium forming manganese (trivalent) hydroxide. When acidified to a pH less than 2.5, the manganese hydroxide dissolved to liberate manganese, which was titrated against a standard thiosulphate (Sodium thiosulphate-Merck) solution using starch as indicator (Grasshoff *et al.,* 1999).

Total alkalinity and Total hardness

Total alkalinity (mg/l) was determined by the amount of sulphuric acid (H_2SO_4) (Merck) neutralized together with a phenolphthalein (Merck) and methyl orange, (Merck) which gave pink colour in the presence of hydroxide and carbonate. Mixed indicator consisting of methyl orange and bromo cresol green (Merck) in which the colour changed from blue green to orange when bicarbonates was titrated with acid. Phenolphthalein gave a pink colour only with hydroxides and carbonates. End point was pink to colourless, at a pH of 8.3. The mixed indicator indicated the bicarbonate titration at a pH of 4.3. Total hardness (mg/l) was determined by complex metric titration using Ethylenediamine Tetra Acetic Acid (EDTA) (Merck). Small amount of Erichrome Black 'T' was added to an aqueous solution containing calcium (Ca^{+2}) and magnesium (Mg^{+2})

ions at a pH of 10 ±0.1 and then the solution turning wine red when titrated against EDTA. All Mg^{+2} and Ca^{+2} formed complexes with the addition of EDTA, the solution turned from wine red to blue Which indicated the end point of the titration (Grasshoff *et al.,* 1999).

Nitrite and Nitrate

Nitrite (mg/l) in seawater was determined by the reaction of aromatic amine, sulfanilamide (Merck) coupled with n-(1-naphthyl)-ethylene diamine dihydrochloride, (Merck) to form an azo dye. The absorbance of the dye was measured spectrophotometrically (Plate 1.6) at 540 nm. Nitrate (mg/l) was reduced to nitrite through cadmium granules (Merck-Cadmium coarse powder, GR of size 0.3-1.6 mm) reduction column. Nitrate was quantitatively reduced to nitrite at the flow rate of 8 ml per minute. The column was washed with ammonia buffer (prepared with 10g of ammonia chloride per litre of distilled water with the addition of ammonia solution till the pH 8.5 is adjusted) after running of every sample. It was then analysed by the aromatic amine, sulfanilamide coupled with n-(1-naphthyl)-ethylene diamine dihydrochloride reaction to form an azo dye which was then measured spectrophotometrically at 540 nm. This concentration was subtracted with the nitrite concentration earlier to acquire the nitrate concentration in seawater (Grasshoff *et al.,* 1999).

Ammonia and Inorganic phosphate

Ammonia (mg/l) was determined based on the blue colour of indophenol formed by phenol and hyperchlorite in presence of nitroprusside (sodium nitroprusside- Merck). This blue colour of indophenol was measured spectrophotometrically at 630 nm. To prevent precipitation of calcium and magnesium hydroxides and carbonates present at a pH higher than 9.6, citrate buffer was added. Inorganic phosphate (mg/l) in seawater was determined by reaction with acid-ammonium molybdate, forming a phosphomolybdate complex, which was reduced by ascorbic acid in the presence of antimonyl ions to a blue coloured complex. The extinction of the blue colour was measured spectrophotometrically at 880 nm using 5cm cell.

To avoid interference by silicate, the pH was kept below one (Grasshoff *et al.,* 1999).

Reactive silicate

Reactive silicate (mg/l) in seawater was allowed to react with acid ammonium molybdate forming a yellow silicomolybdic acid, which was reduced by ascorbic acid in presence of oxalic acid (to prevent interference from phosphate) to develop blue coloured complex. The extinction of the blue colour was measured spectrophotometrically at 810 nm using 1 cm cells. All standards were prepared and standardized following (Grasshoff *et al.,* 1999). The assessment of the water quality parameters was carried out following the standards of Australian and New Zealand Environment and Conservation Council (ANZEEC, 2000)

Statistical analysis

PASW (Predictive analytical software) (SPSS) version 18 was used to study the correlation statistics between water quality parameters. PRIMER (Plymouth routines in multivariate ecological research) version 6 (6.1.7) was used to study the parameters through draftsman plot (Clarke and Gorley, 2006).

RESULTS AND DISCUSSION

All through post-monsoon, summer, pre-monsoon and monsoon, pH, salinity, total hardness and total alkalinity varied with respect to tidal and riverine influences. Temperature showed significant seasonal variation (P<0.05). Amakiri (2006) reported 27.6°C in wet season and 31.6°C in dry season. Ekeh and Sikoki (2003) reported lowest temperature of 25°C in the wet season and 30°C in the dry season at New Calabar. In the present study the temperature in post-monsoon was high when compared to summer and monsoon (Table 1, 2 and 4)Temperature showed a negative correlation with pH, salinity and total hardness, meanwhile pH, dissolved oxygen, salinity and total hardness also showed a negative correlation with nutrients and heavy metals (Table 5, 6, 7 and 8) (*P*<0.01) (α=0.05), might be due to release of industrial and municipal sewage along the stations 4 and 3 and influence of seawater along the stations 1 and 2

Table 1. Water quality parameters of postmonsoon season in Ennore creek

Parameters	Station 1	Station 2	Station 3	Station 4	ANZEEC, 2000
Temperature (°C)	26.33 ±0.58	28.00 ±1.00	29.33 ±1.53	31.33 ±2.08	30
pH	7.93 ±0.06	7.70 ±0.10	6.55 ±0.37	6.14 ±0.08	6.0 – 9.0
Dissolved oxygen (mg/l)	5.23 ±0.40	3.77 ±0.15	3.60 ±0.17	2.49 ±0.47	>5.0
Salinity (PSU)	32.45 ±0.81	28.47 ±0.95	22.32 ±1.00	21.90 ±0.76	NA
Total hardness (mg/l)	1758.67 ±190.59	1670.67 ±147.86	1545.00 ±87.22	1247.80 ±59.44	NA
Total alkalinity (mg/l)	127.17 ±40.87	120.33 ±31.66	132.33 ±11.36	19.50 ±0.87	≥ 20
Nitrite (mg/l)	0.21 ±0.10	0.40 ±0.07	0.68 ±0.13	1.10 ±0.09	<0.10
Nitrate (mg/l)	4.47 ±0.65	9.30 ±0.50	12.09 ±1.56	13.28 ±1.04	<100
Inorganic phosphate (mg/l)	0.19 ±0.12	0.13 ±0.07	0.91 ±0.20	1.09 ±0.16	<0.05
Ammonia (mg/l)	0.53 ±0.21	0.72 ±0.17	1.71 ±0.40	1.68 ±0.53	<1.0
Reactive silicate (mg/l)	7.97 ±1.43	5.58 ±1.13	17.17 ±2.54	19.95 ±1.24	NA

*Correlation was significant (α=0.05) at the *P*<0.0001 (2-tailed) between stations of all parameters, highly significant; ANZECC - Australian and New Zealand Environment and Conservation Council; NA-Not available; Values are mean and standard deviation of n=6

Table 2. Water quality parameters of summer season in Ennore creek

Parameters	Station 1	Station 2	Station 3	Station 4	ANZEEC, 2000
Temperature (°C)	28.00 ±1.00	28.00 ±1.00	29.33 ±2.52	29.33 ±1.53	30
pH	8.02 ±0.12	7.77 ±0.15	6.83 ±0.24	5.91 ±0.28	6.0 – 9.0
Dissolved oxygen (mg/l)	4.07 ±0.08	4.23 ±0.91	2.53 ±0.55	2.72 ±0.40	>5.0
Salinity (PSU)	33.70 ±0.43	29.18 ±0.35	21.69 ±0.55	21.44 ±0.72	NA
Total hardness (mg/l)	1924.17 ±25.04	1928.33 ±47.52	1753.33 ±42.39	1457.50 ±200.71	NA
Total alkalinity (mg/l)	121.83 ±28.02	121.67 ±28.29	126.83 ±2.31	17.83 ±1.89	≥ 20
Nitrite (mg/l)	0.10 ±0.04	0.15 ±0.07	0.58 ±0.15	1.15 ±0.30	<0.10
Nitrate (mg/l)	3.93 ±0.55	5.83 ±1.74	13.79 ±2.32	19.76 ±2.84	<100
Inorganic phosphate (mg/l)	0.23 ±0.22	0.27 ±0.17	0.91 ±0.64	1.86 ±0.27	<0.05
Ammonia (mg/l)	0.20 ±0.11	1.58 ±0.62	1.64 ±0.72	2.46 ±0.73	<1.0
Reactive silicate (mg/l)	7.47 ±0.71	5.20 ±1.15	17.70 ±1.31	22.59 ±1.58	NA

* Correlation was significant (α=0.05) at the *P*<0.0001 (2-tailed) between stations (1, 2 and 3, 4) of all parameters, highly significant; ANZECC - Australian and New Zealand Environment and Conservation Council; NA-Not available; Values are mean and standard deviation of n=6

Table 3. Water quality parameters of premonsoon season in Ennore creek

Parameters	Station 1	Station 2	Station 3	Station 4	ANZEEC, 2000
Temperature (°C)	28.67 ±1.53	28.67 ±0.58	29.33 ±1.53	29.00 ±1.00	30
pH	7.87 ±0.06	7.50 ±0.20	6.55 ±0.50	6.16 ±0.06	6.0 – 9.0
Dissolved oxygen (mg/l)	4.57 ±0.50	4.60 ±0.43	2.87 ±0.68	2.97 ±0.32	>5.0
Salinity (PSU)	34.51 ±0.18	27.56 ±0.58	20.14 ±1.17	18.83 ±1.96	NA
Total hardness (mg/l)	1939.25 ±63.85	1832.50 ±22.22	1566.50 ±73.83	1178.00 ±94.32	NA
Total alkalinity (mg/l)	153.58 ±14.92	150.42 ±7.01	99.83 ±9.81	16.50 ±2.29	≥ 20
Nitrite (mg/l)	0.19 ±0.10	0.27 ±0.17	1.88 ±0.50	1.43 ±0.22	<0.10
Nitrate (mg/l)	4.37 ±0.93	4.60 ±0.89	19.62 ±1.54	18.48 ±5.75	<100
Inorganic phosphate (mg/l)	0.36 ±0.23	0.18 ±0.13	1.98 ±0.34	1.59 ±1.08	<0.05
Ammonia (mg/l)	0.13 ±0.05	0.94 ±0.06	2.60 ±0.78	1.07 ±0.67	<1.0
Reactive silicate (mg/l)	5.86 ±0.42	5.50 ±0.88	18.81 ±1.25	32.89 ±1.52	NA

* Correlation was significant (α=0.05) at the *P*<0.0001 (2-tailed) between stations of all parameters, highly significant; ANZECC - Australian and New Zealand Environment and Conservation Council; NA-Not available; Values are mean and standard deviation of n=6

system, which may influence the physico-chemical characteristics and also the distribution and abundance of flora and fauna. Higher temperature values recorded in the dry months are expected since heat from sunlight. Similarly the drop in

Dissolved oxygen, ammonia concentrations in stations 1 and 2 were below the permissible limits of Australian and New Zealand Environment and Conservation Council (ANZEEC) during postmonsoon, summer, premonsoon and monsoon
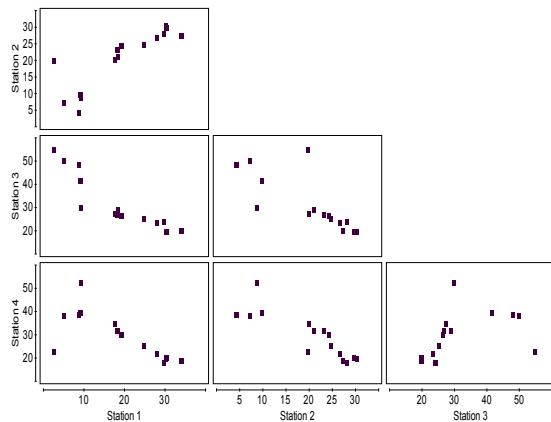
findings, Das and Acharya (2003) reported low

Fig. 2. Draftsman plot of the water quality parameters exhibiting the strong correlation between the station 1 and 2 (r^2= 0.998) (α=0.05) at *P*<0.0001 (2-tailed), between station 3 and 4 (r^2= 0.999) (α=0.05) at *P*<0.0001 (2-tailed) in Ennore creek of all seasons

dissolved oxygen of 3.8 and 2.1 mg/l in rainy season, which decreased to 1.7 mg/l and 1.2 mg/l in summer of Kathajodi river at Cuttack city. A possible explanation for the lower mean dissolved oxygen values in the wet season could be the turbidity nature of the water, due to inflows from run-offs and decomposition of organic matter in the water (Braide *et al.,* 2004). Singh *et al.* (2004) reported the average dissolved oxygen concentration of Gomti river in Pipraghat region ranging from nil to 5.4 mg/l, due to the flow of urban drains into the river. Dissolved oxygen was negatively correlated (*P*<0.01) (α=0.05) with temperature because the solubility of oxygen in water decreases with increasing temperature. Oxygen-depleted water columns impact benthic communities by producing acute changes in the distribution, abundance, and diversity of species

Table 4. Water quality parameters of monsoon season in Ennore creek

Parameters	Station 1	Station 2	Station 3	Station 4	ANZEEC, 2000
Temperature (°C)	26.33 ±0.58	27.33 ±0.58	28.00 ±1.00	29.00 ±1.00	30
pH	7.71 ±0.10	7.10 ±0.10	6.08 ±0.06	5.71 ±0.25	6.0 – 9.0
Dissolved oxygen (mg/l)	5.91 ±0.30	4.68 ±0.06	2.15 ±0.05	2.12 ±0.08	>5.0
Salinity (PSU)	29.08 ±1.17	25.66 ±1.52	18.58 ±2.25	14.47 ±1.21	NA
Total hardness (mg/l)	1340.34 ±442.36	1358.00 ±362.83	1080.83 ±140.71	785.32 ±240.62	NA
Total alkalinity (mg/l)	128.94 ±24.68	124.00 ±3.91	68.67 ±5.53	9.50 ±1.00	≥ 20
Nitrite (mg/l)	0.06 ±0.04	1.25 ±0.34	4.24 ±1.11	4.05 ±0.80	<0.10
Nitrate (mg/l)	5.04 ±0.65	7.99 ±0.72	33.23 ±2.36	22.30 ±1.06	<100
Inorganic phosphate (mg/l)	1.06 ±0.38	1.30 ±0.15	3.25 ±0.43	4.55 ±1.30	<0.05
Ammonia (mg/l)	1.28 ±0.89	3.35 ±0.53	4.94 ±0.51	6.42 ±0.33	<1.0
Reactive silicate (mg/l)	7.45 ±0.62	7.18 ±1.87	24.43 ±1.22	36.88 ±7.04	NA

* Correlation was significant (α=0.05) at the *P*<0.0001 (2-tailed) between stations of all parameters, highly significant; ANZECC - Australian and New Zealand Environment and Conservation Council; NA-Not Available; Values are mean and standard deviation of n=6

Table 5. Correlation matrix between the water quality parameters of the four stations in Ennore creek during the postmonsoon season

	Temperature	pH	Dissolved oxygen	Salinity	Total hardness	Total alkalinity	Nitrite	Nitrate	Inorganic phosphate	Ammonia	Silicate
Temperature	1										
pH	-0.95*	1									
Dissolved oxygen	-0.97*	0.86	1								
Salinity	-0.93	0.96*	0.89	1							
Total hardness	-0.97*	0.93	0.92	0.85	1						
Total alkalinity	0.50	-0.73	-0.29	-0.62	-0.53	1					
Nitrite	0.99**	-0.96*	-0.94	-0.91	-0.99*	0.56	1				
Nitrate	0.95	-0.91	-0.96*	-0.97*	-0.85	0.43	0.91	1			
Inorganic phosphate	0.90	-0.99*	-0.77	-0.92	-0.89	0.83	0.92	0.84	1		
Ammonia	0.89	-0.98*	-0.80	-0.98*	-0.83	0.77	0.88	0.91	0.97*	1	
Silicate	0.86	-0.97*	-0.72	-0.89	-0.87	0.87	0.89	0.78	1.00**	0.95	1

*Correlation is significant at the 0.05 level (2-tailed);**Correlation is significant at the 0.01 level (2-tailed)

Table 6. Correlation matrix between the water quality parameters of the four stations in Ennore creek during the summer season

	Temperature	pH	Dissolved oxygen	Salinity	Total hardness	Total alkalinity	Nitrite	Nitrate	Inorganic phosphate	Ammonia	Silicate
Temperature	1										
pH	-0.91	1									
Dissolved oxygen	-0.99**	0.86	1								
Salinity	-0.95*	0.91	0.92	1							
Total hardness	-0.84	0.98*	0.78	0.80	1						
Total alkalinity	-0.22	0.59	0.13	0.23	0.72	1					
Nitrite	0.88	-0.99**	-0.83	-0.86	-1.00**	-0.66	1				
Nitrate	0.94	-1.00**	-0.89	-0.93	-0.97*	-0.53	0.99*	1			
Inorganic phosphate	0.86	-0.99*	-0.81	-0.83	-1.00**	-0.69	1.00**	0.98*	1		
Ammonia	0.71	-0.85	-0.63	-0.87	-0.79	-0.51	0.82	0.85	0.81	1	
Silicate	0.96	-0.96*	-0.94	-0.89	-0.94	-0.45	0.96*	0.97*	0.95	0.71	1

*Correlation is significant at the 0.05 level (2-tailed); **Correlation is significant at the 0.01 level (2-tailed)

Table 7. Correlation matrix between the water quality parameters of the four stations in Ennore creek during the premonsoon season

	Temperature	pH	Dissolved oxygen	Salinity	Total hardness	Total alkalinity	Nitrite	Nitrate	Inorganic phosphate	Ammonia	Silicate
Temperature	1										
pH	-0.78	1									
Dissolved oxygen	-0.90	0.96*	1								
Salinity	-0.80	0.97*	0.91	1							
Total hardness	-0.59	0.96*	0.87	0.89	1						
Total alkalinity	-0.92	0.96*	1.00**	0.93	0.86	1					
Nitrite	0.97*	-0.90	-0.97*	-0.90	-0.76	-0.98*	1				
Nitrate	0.93	-0.95*	-1.00**	-0.92	-0.85	-1.00**	0.99*	1			
Inorganic phosphate	0.96*	-0.89	-0.98*	-0.85	-0.76	-0.98*	0.99**	0.99*	1		
Ammonia	0.92	-0.64	-0.72	-0.75	-0.40	-0.76	0.86	0.77	0.80	1	
Silicate	0.62	-0.95	-0.90	-0.85	-0.99*	-0.88	0.78	0.87	0.80	0.38	1

*Correlation is significant at the 0.05 level (2-tailed); **Correlation is significant at the 0.01 level (2-tailed)

Table 8. Correlation matrix between the water quality parameters of the four stations in Ennore creek during the monsoon season

	Temperature	pH	Dissolved oxygen	Salinity	Total hardness	Total alkalinity	Nitrite	Nitrate	Inorganic phosphate	Ammonia	Silicate
Temperature	1										
pH	-0.97*	1									
Dissolved oxygen	-0.93	0.99*	1								
Salinity	-0.98*	0.99**	0.97*	1							
Total hardness	-0.92	0.91	0.86	0.95*	1						
Total alkalinity	-0.93	0.97*	0.96*	0.99*	0.96*	1					
Nitrite	0.90	-0.98*	-1.00**	-0.96*	-0.84	-0.95*	1				
Nitrate	0.71	-0.86	-0.92	-0.82	-0.68	-0.85	0.94	1			
Inorganic phosphate	0.95	-0.97*	-0.93	-0.99*	-0.99*	-0.99**	0.92	0.78	1		
Ammonia	1.00**	-0.99*	-0.95*	-0.98*	-0.90	-0.94	0.94	0.77	0.94	1	
Silicate	0.93	-0.94	-0.90	-0.97*	-0.99**	-0.99*	0.89	0.75	1.00**	0.92	1

*Correlation is significant at the 0.05 level (2-tailed); **Correlation is significant at the 0.01 level (2-tailed)

(Raffaelli, 2000). There was significant negative correlation between salinity and temperature. Ayoade *et al.* (2006) reported that dissolved oxygen concentration at Asejire lake attained its peak at the height of rainy season. The lower dissolved oxygen downstream also implies that the rivers were more polluted downstream. The salinity was negatively correlated to silicate and nitrite. The concentration of nutrients decreased with higher salinity.

Ouyang *et al.* (2006) reported that the water temperature had weak correlations with alkalinity and salinity which were, in general, similar to our findings. The total alkalinity in the station 4 during premonsoon and monsoon was 16.50 mg/l, below the permissible limits of ANZECC (Table 3). It is understandable that domestic wastewater from untreated or overflow sewer pipes constituted a major pollution source for the monitoring sites in values of dissolved oxygen and pH. Hydrolysis of these acidic materials causes a decrease of water pH value (Singh *et al.,* 2004). pH was lower in stations 3 and 4 than stations 1 and 2. Highest pH values were recorded in the dry season and lower values of pH in the late rainy season. Similar trend was also reported by Ekeh and Sikoki (2003) in the New Calabar river. In the present study, pH showed a positive correlation ($P<0.05$) ($\alpha=0.05$) with temperature, dissolved oxygen, salinity and total hardness, but showed negative correlation ($P<0.01$) ($\alpha=0.05$) with nutrients and total alkalinity (Table 5, 6, 7 and 8) may be due to the influx and decay of debris in the area as well as imbalanced level of H^+ ions from surface run-offs during the monsoon (Singh *et al.,* 2004). They indicate the importance of mixing between polluted freshwaters and costal saline waters. Negative correlation ($P<0.05$) ($\alpha=0.05$) between nutrients and salinity demonstrate that land sources are the

in stations 1 and 2 in the surface waters. Silicate is associated with land-based resources with concentration higher in rainy season than in dry season (Wu and Wang, 2007). Nutrients concentrations in all stations during postmonsoon, summer, premonsoon and monsoon were above the permissible limits, sources are being anthropogenic activities in all the stations, especially the Araniyar and Korttalaiyar river contributing the industrial effluents and domestic sewage in stations 3 and 4 (Paranhos *et al.,* 1998).

During postmonsoon, summer, premonsoon and monsoon the correlation was significant between stations 1 and 2 (r^2=0.998) (α=0.05) at *P*<0.0001, station 3 and 4 (Fig 2). Studies show that excess utilization of fertilizer in agriculture and sewage discharge result in the increase of nitrogen and phosphorous in the estuary (Adeyemo, 2003). Nitrite is the main form of dissolved inorganic nitrogen followed by ammonia and nitrate in the process of nitrification (Wang *et al.,* 2006). As long as nitrification is stirring in the water, an increase in nitrite and a reduction in ammonia is a normal event (Wu and Wang, 2007). In the present study the nitrate value was 22.3 mg/l which is rather less than reported by Luiza *et al.* (1999) of 58 mg/l at Piracicaba river in Brazil. During summer, nutrients except nitrate in all the stations of the Ennore creek were above the permissible limits in premonsoon and monsoon (Table 2). High levels of both phosphates and nitrates can lead to eutrophication ultimately reducing dissolved oxygen levels in water (Stimson *et al.,* 2001). Olajire and Imeokparia (2001) reported that nitrate concentration in Osun river, Nigeria varied from 14 to 20 mg/l.

Helen *et al.* (2005) reported that nitrate were 21 to 24 mg/l, at upper Thames basin, in southern England. Mladenov *et al.* (2005) reported nitrate being two times higher in Notwane river in south-eastern Botswana. Das and Acharya (2003) reported that nitrate concentration varied from 14 to 126 mg/l in Kathajodi river in winter and 173 and 155 mg/l in rainy reason. Ravindra *et al.* (2005) reported nitrate in winter and summer

seasons were 5 and 9 mg/l, respectively at Yamuna (2001) reported that phosphates of 0.46 and 0.59 mg/l in Osun river, Nigeria. Mladenov *et al.* (2005) reported phosphates in treated sewage of 3.65 mg/l at Notwane river in south-eastern Botswana. In the present investigation, ammonia was high in stations 3 and 4; may be due to the death and subsequent decomposition of phytoplankton and excretion of ammonia by planktonic organisms (Rajasegar, 1998).

CONCLUSION

In the present study the water quality parameters in the Ennore creek showed that concentrations of nutrients were above permissible limits of ANZEEC, the creek is polluted. The creek was under pressure from stations 1, 2, 3 and 4. High concentrations of nutrients were contributed by the industrial and domestic sewage in stations 3 and 4. Water quality forms the basic intuition for the life sustaining medicine for propagation of aquatic organisms especially to juveniles. This is the first study involving the seasonal variation in water quality parameters, the study involving the heavy metal distributions in water, sediment and tissues are in progress.

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