

# Seasonal variation in physicochemical properties of coastal waters in Southeast Coast of India with special emphasis on nutrients

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## ABSTRACT

A study pertaining to the seasonal variation in physicochemical properties of the coastal waters, in summer, winter and monsoon seasons in Rameswaram and Tuticorin, Southeast coast of Tamil Nadu, India, was carried out for a period of 1 year from March 2014 to February 2015. The principal component analysis (PCA) of the physicochemical variables identified the Rameswaram and Tuticorin from the two component possible groups, which were responsible for the data structure, explaining the Rameswaram % total variance 93.26 and also Tuticorin % total variance 95.99 of the data set. In Rameswaram was component 1 to the % total variance (54.23%) and component 2 (39.03). A correlation matrix positively loading of the variables was computed to axis 1 were represented to WT (Water temperature), TP (Total Phosphorus), SP (Sulphate) and Mg (Magnesium) during at summer season while with negatively loading of the parameters in axis 1 were represented by pH, DO, BOD, Cl, NO<sub>3</sub><sup>-</sup>, NH<sub>3</sub> and Ca with also negatively loading with component 2 variable to WT, Cl, NH<sub>3</sub> and TP while also to positively loading axis 2 were represented to pH, RF, DO, BOD, NH<sub>3</sub>, SO<sub>4</sub><sup>2-</sup>, Ca and Mg during at winter season. And monsoon and negatively loading WT, Cl, NH<sub>3</sub> and TP. In TN was component 1 to the % total variance (53.95%) and component 2 (42.04%). A correlation matrix positively loading of the variables was computed to axis 1 were represented to pH, RF and NH<sub>3</sub> at monsoon season and negatively loading WT, DO, BOD, Cl, NH<sub>3</sub>, TP, SO<sub>4</sub><sup>2-</sup>, Ca and Mg at summer and also axis 2 were represented to positively loading variables in WT, DO, BOD, Cl, NH<sub>3</sub>, and SO<sub>4</sub><sup>2-</sup>, at summer and winter season. Negatively loading to variables in pH, RF, TP, Ca and Mg at summer and monsoon. Nutrients enrichments observed close to the major urban area in Tuticorin coast are associated with the industrialized activities areas. The higher concentration comparing Tuticorin region than the Rameswaram.

**Keywords:** Physico- chemical properties; PCA; South East Coast of Tamil Nadu.

## INTRODUCTION

Physicochemical parameters of coastal water control the dynamics and structure of the phytoplankton of aquatic ecosystem (Hulyal and Kaliwal, 2009). There are several sources which are liable to change the biodiversity of a particular area. Hydro- biological studies have shown that urbanization is the root cause of water pollution (Sinha and Shrivastava 1992). Pigments distribution also affected by particular environmental conditions, such as light and nutrients and has an important effect on indicator pigment to chlorophyll *a* concentrations (Descy et al., 2000). Multivariate statistical techniques have been applied to characterize and assess freshwater quality; they are beneficial in verifying temporal and spatial variations affected by natural and anthropogenic factors linked to seasonality (Helena et al., 2000; Singh et al., 2005; Shrestha and Kazama, 2007). Principal component analysis (PCA) was developed to summarize and make easier the analysis of multivariate data sets (Gauch, 1989). PCA technique was earlier used alone or in combination with other approaches, to simplify the interpretation of the relationship within complex data-set and ideal aquatic, environmental, and ecological processes (Camdevyren et al., 2005 and Te et al., 2011). Only few studies focused on seasonal variations of phytoplankton communities in the industrial polluted site compared with less polluted site. Hence the present study was designed to investigate the changes of physico-chemical parameters and nutrients in Rameswaram (RA) and Tuticorin (TN), in Southeast coast of Tamil Nadu, India

## MATERIALS AND METHODS

### Study Area and Sample collection site

The study area one, falls within the geographical coordinates 9° 13' 50" E and 79° 11' 55" N and study area two falls within the geographical coordinates 8° 46' 15" E and 78° 10' 7" N were selected as reference and polluted site respectively (Location map).

Seawater samples were collected from Rameswaram (RA) and Tuticorin (TN) area southeast coast of India (Fig. 1). Four months make one season. March to June, represented summer season, July to October represented monsoon season, and November to February the winter season. Gulf of Mannar in the southeast coast of India covers from Rameswaram Island in the north to Kanyakumari in the south. The Gulf of Mannar was set up on 18<sup>th</sup> February 1989 jointly by the Government of India and the state of Tamil Nadu. Coastal location in Tuticorin is well known for pearl, fishery and shipbuilding. It is one of the important

major ports having a number of ship movements. The movement of ships and fishing operation by mechanized boats release oil effluents and petrochemical products into the seawater. The Thermal power station directly dumps its ash into the sea.

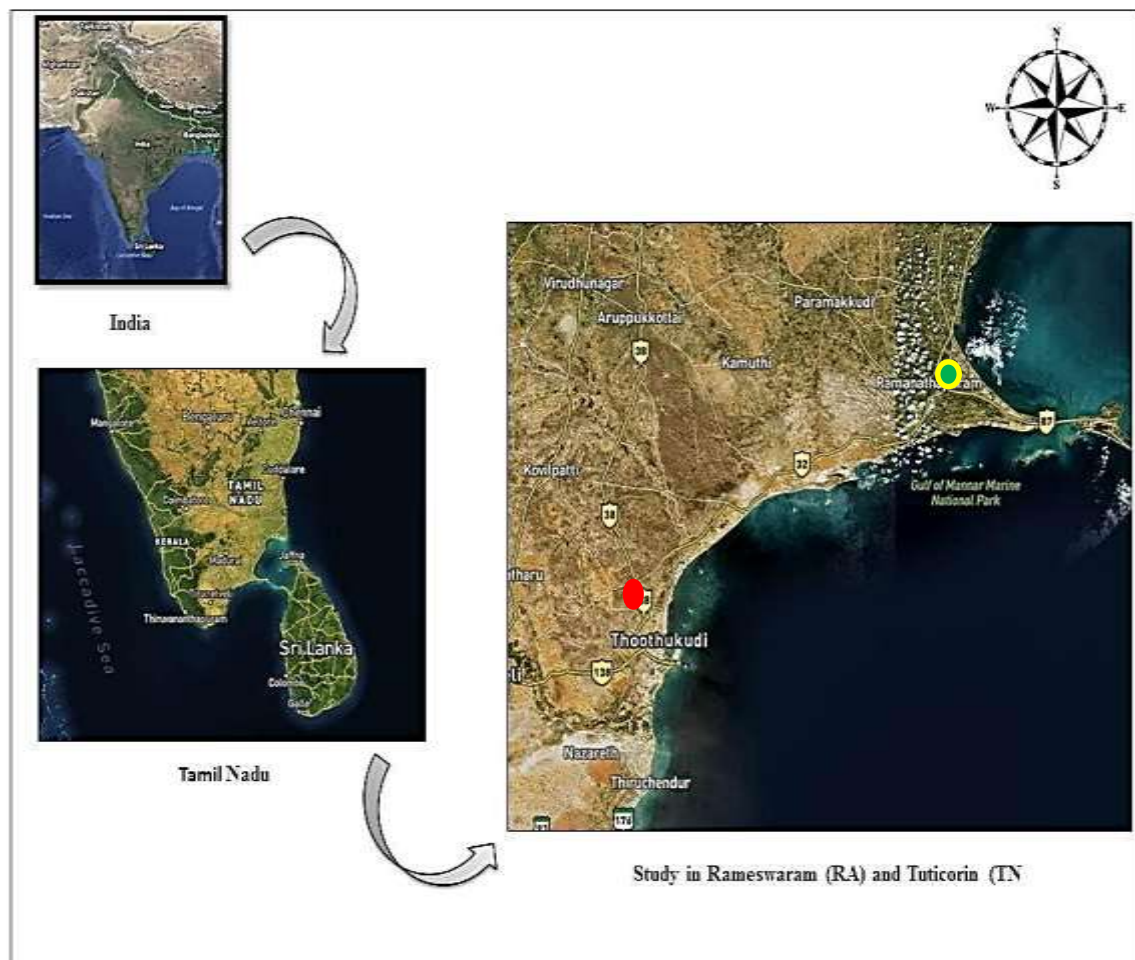


Fig.1 Sampling area in RA and TN of Gulf Mannar south east coast of India

### Physicochemical parameter analysis:

Analysis of physicochemical parameters such as pH was measured using a Elico pH meter (Model LC- 120). Water temperature was measured using a standard Celsius Thermometer. The rainfall data used in this study were obtained from Regional Meteorological Department, Chennai from the year 2014 to 2015. Dissolved oxygen was estimated by the modified Winkler's method. For the analysis of nutrients, surface water samples were collected in clean polythene bottles and kept in an ice box and transported to the laboratory. The water samples were filtered using a whatman filter paper (MFS) and analyzed for dissolved oxygen (DO), biological oxygen demand (BOD), chloride ( $\text{Cl}^-$ ), nitrate ( $\text{NO}_3^-$ ), ammonia ( $\text{NH}_3$ ), total phosphorus (TP), sulphate ( $\text{SO}_4^{2-}$ ), calcium (Ca) and magnesium (Mg) by standard procedure (Strickland and Parsons, 1972).

### Statistical Analysis

Multivariate principal components analysis (PCA) was carried out to visually explore patterns of associations among the physicochemical variables and between variables and the sampling sites using STATISTICA for windows (Version 10) software. In addition to the multivariate analysis, data analysis and validation were made using SPSS (Version 16). Correlation coefficient variance analysis was done using the R Studio (Version 3.4.1)

## RESULTS AND DISCUSSION

Monitoring the fluctuations of hydrographic properties in seawater of coral reef islands, Gulf of Mannar (Yogeshkumar and Geetha, 2012). Physico-chemical parameters, species composition and seasonal variant in phytoplankton richness have been detailed in other regions of Indian coastal waters (Saravanakumar et al., 2008). The pH indicates the intensity of the acidic or basic character of a solution and is measured by the dissolved chemical compounds and biochemical processes in the solution. Usually variations in pH values during changed seasons of the year is attributed to factors like removal of  $\text{CO}_2$  in photosynthesis, through bicarbonate degradation, fall of seawater by freshwater influx, reduction of salinity, temperature and decomposition of organic matter (Upadhyay, 1988; Rajasegar 2003 and Saravanakumar et al., 2008). The lowest pH value was recorded (7.56) in summer season at TN and highest (7.80) in monsoon season at TN. Related seasonal pattern was verified earlier (Thangaraj,

1984; Palpandi, 2011). The seasonal variations in the water temperature maybe associated with the wind force, freshwater discharge entry of the inshore water and atmospheric temperature. The reduction in the water temperature essentially depends upon the intensity of rainfall during monsoon and the low air temperature existed at the time. Related observations have been described by (Thangaraj, 1984) in Vellar estuary; (Senthilnathan, 1990) in Vellar.

The water temperature values in RA ranged between 33.66 to 26 ° C and in TN ranged from 35 to 28° C. The water temperature value was maximum RA (35 ° C) during the summer. Minimum water temperature value at TN 26 ° C during the season of monsoon. Related observed as it has been verified by some earlier investigators (Anandan, 1995 and Prabhahar, 2000). A smaller wave and tidal action with decreased freshwater entry and land drainage may also be measured fluctuations (Sampathkumar and Kannan, 1998). Rainfall is the greatest significant cyclical phenomenon in tropical countries as it brings about important changes in the physical and chemical characteristics of the coastal environment. The overall rainfall values in RA ranged between 643.33 to 46.33 mm and in TN ranged from 459.33 to 23.67 mm. The total rainfall value was maximum RA 643.33 mm during the monsoon. Minimum total rainfall value at TN 23.67 mm during the season of monsoon. The rainfall in India is mostly influenced by binary monsoons viz., southeast monsoon on the west coast and northeast monsoon on the east coast (Perumal, 1993). The dissolved oxygen is very vital for the respiratory metabolism of all aquatic animals. The dissolved oxygen play a role of regulator of metabolic activities of organisms and thus governs metabolism of the biological community as a total and used as an indicator of trophic status of the water. It may be current in water due to direct distribution from air and photosynthetic movement of autotrophs. The DO values in RA ranged between 4.1 to 4.53 mg/L and in TN ranged from 2.95 to 4.54mg/L. The DO value was maximum TN (4.54mg/L) during the summer. Minimum DO value at TN (2.95 mg/L) during the season of monsoon.

Higher dissolved oxygen concentration observed during the monsoon season might be due to the cumulative effect of greater wind velocity joined with heavy rainfall and the resultant freshwater mixing (Mishra et al., 1993 and Das et al., 1997). BOD is a quantity of organic material pollution in water. BOD is the total of dissolved oxygen vital for the biochemical decay of organic compounds and the oxidation of convinced inorganic materials. The BOD values in RA ranged between 6.56 to 13.91 mg/L and in TN ranged from 3.73 to 25.06 mg/L. The BOD value was maximum TN (25.06 mg/L) during the summer. Minimum BOD value at TN (3.73 mg/L) during the season of monsoon. Seasonal changes in BOD with low values during wet seasons (rainy) may be increased surface run-offs, soil erosions and effluents release into the receiving water bodies by (Oyewo et al., 1999). Chloride is a ubiquitous aqueous anion in all natural waters, the concentrations varying very commonly and reaching a maximum in sea water. Cl values in RA ranged between 18.36 to 20.67 g/L and in TN ranged from 20.19 to 22.42 g/L. The Cl value was maximum TN (22.42 g/L) during the summer. Minimum Cl value at RA (18.36g/L) during the season of winter. The most important sources of chloride in the natural waters are sediments (Mishra et al. 2008). Higher chloride content is an indication of pollution, which is due to either the organic wastes or the industrial effluents (Ambasht and Tripathi, 1978; Rai and Tripathi, 2006). Nitrate is one of the most significant nutrient which accounts for the productivity in water.

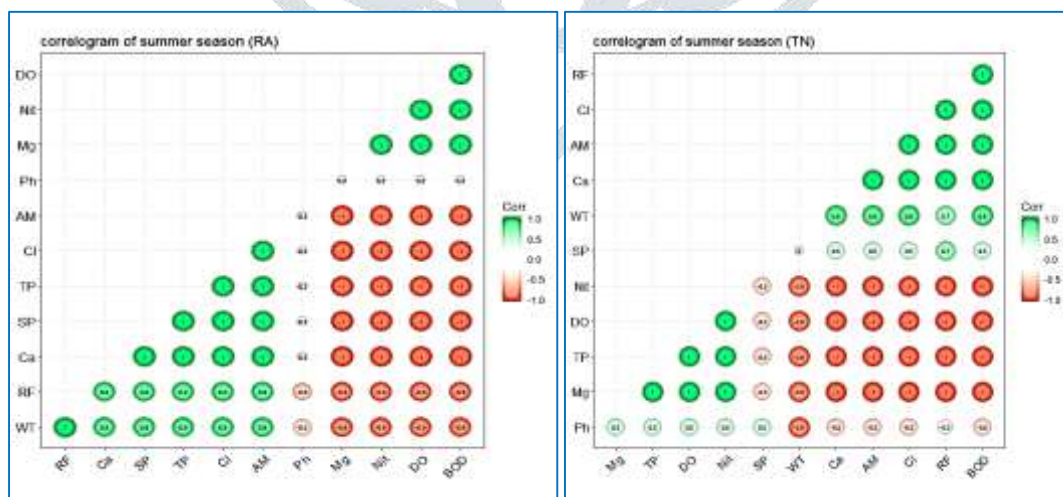
The  $\text{NO}_3^-$  values in RA ranged between 76.12 to 121.88  $\mu\text{M/L}$  and in TN ranged from 96.66 to 124.59  $\mu\text{M/L}$ . The  $\text{NO}_3^-$  value was maximum TN (124.59  $\mu\text{M/L}$ ) during the winter season. Minimum  $\text{NO}_3^-$  value at RA (76.12  $\mu\text{M/L}$ ) during the season of summer. The increased nitrates level was due to fresh water entry and terrestrial run-off in the monsoon period. Another probable way of nitrates entry is through oxidation of ammonia form of nitrogen to nitrite formation (Rajasegar, 2003). The recorded low values during non-monsoon period may be due to its utilization by phytoplankton as verified by high photosynthetic activity and also due to the neritic water dominance, which contained only small amount of nitrate (Das et al., 1997; Govindasamy et al., 1992). The most essential source of ammonia in water bodies is the ammonification of organic matter. In higher concentrations ammonia becomes harmful to fishes and other biota. The  $\text{NH}_3$  values in RA ranged between 75.67 to 99.65  $\mu\text{M/L}$  and in TN ranged from 105.93 to 149.37  $\mu\text{M/L}$ . The  $\text{NH}_3$  value was maximum TN (149.37  $\mu\text{M/L}$ ) during the winter. Minimum  $\text{NH}_3$  value at RA (75.67  $\mu\text{M/L}$ ) during the season of winter (Table. 1). The detailed higher concentration could be partially due to the death and subsequent decomposition of phytoplankton and also due to the excretion of ammonia by planktonic organisms.

The documented higher concentration could be partially due to the death and subsequent decomposition of phytoplankton and also due to the excretion of ammonia by planktonic organisms (Kawabata et al., 1993). Phosphorous is considered to be the most important component among the nutrients responsible for eutrophication of a water body. Phosphate is the most vital nutrient for the production of phytoplankton in freshwater which is the primary food for several of the commercial fishes. The TP values in RA ranged between 0.32 to 0.38  $\mu\text{M/L}$  and in TN ranged from 0.52 to 0.85  $\mu\text{M/L}$ . The TP value was maximum TN (0.85  $\mu\text{M/L}$ ) during the monsoon. Minimum TP value at RA (0.32  $\mu\text{M/L}$ ) during the season of winter. The overall phosphate from bottom mud into the water column by turbulence and mixing also attributed to the higher monsoon values. The lesser summer value could be attributed to the limited flow of freshwater, high salinity and utilization of phosphate by phytoplankton (Rajasegar, 2003). The  $\text{SO}_2^{4-}$  values in RA ranged between 215.43 to 231.77 mg/L and in TN ranged from 235.84 to 281.47 mg/L. The  $\text{SO}_2^{4-}$  value was maximum TN (281.47 mg/L) during the winter. Minimum  $\text{SO}_2^{4-}$  value at RA (215.43 mg/L) during the season of monsoon. The higher sulphate concentration is a typical of brackish water (Asonye et al., 2007) which supports the results of this study. The Ca values in RA ranged between 367.33 to 401.74 mg/L and in TN ranged from 464.56 to 508.63 mg/L. The Ca value was maximum TN (508.63 mg/L) during the summer. Minimum Ca value at RA (367.33 mg/L) during the season of summer. The Mg values in RA ranged between 120.78 to 136.95 mg/L and in TN ranged from 149.33 to 167.42 mg/L. The Mg value was maximum TN (167.42 mg/L) during the summer. Minimum Mg value at RA (120.78 mg/L) during the season of monsoon. The variation in calcium and magnesium concentrations may be related to the geology of the area, climate and seasonal variations, dissimilar biogeochemical activities in the water ecosystem, human activities, water uses and due to the addition of surface run-off from agricultural and other catchment area (Kumar et al., 2006). Similar conclusions are made by (Toma, 2000; Raof, 2002).



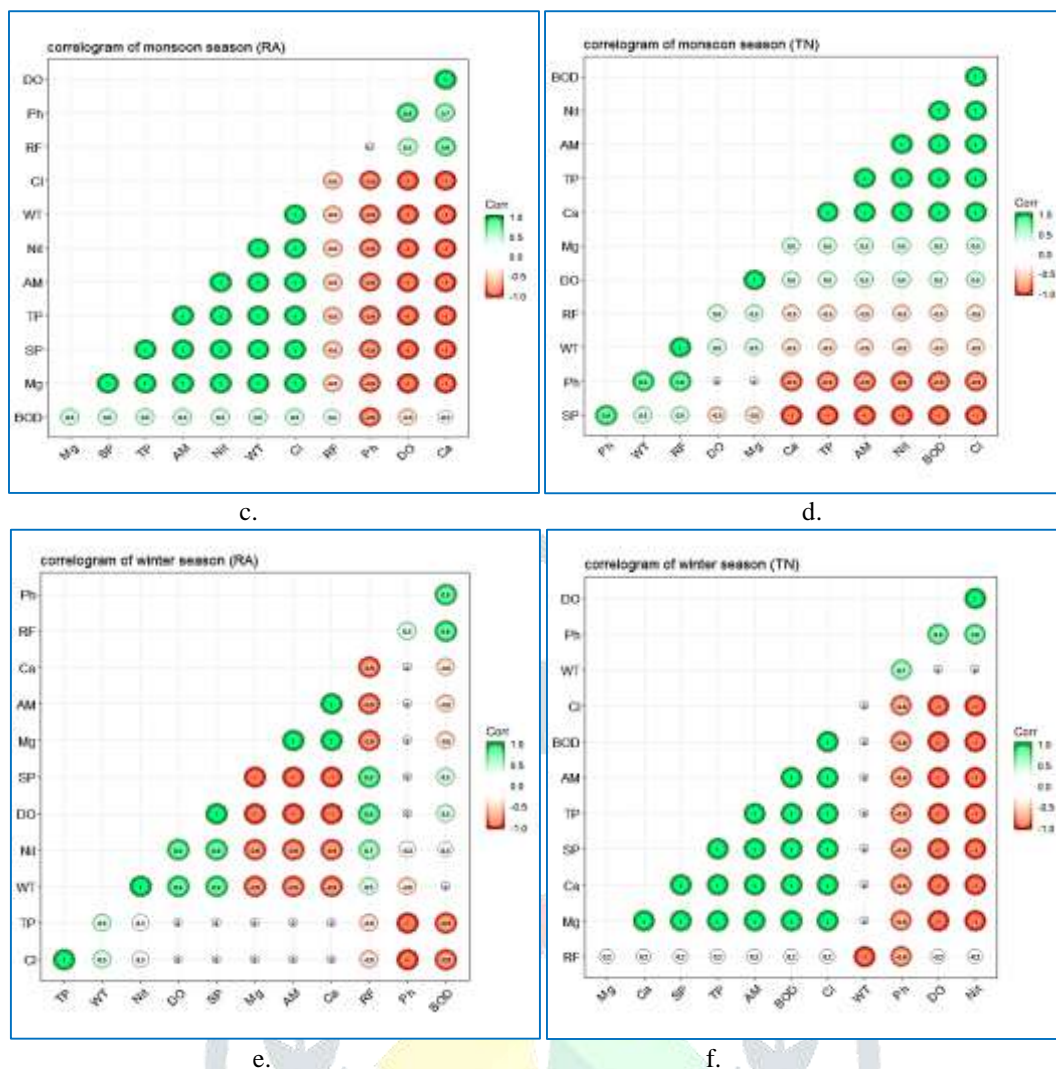
Table 1. Mean of seasonal and annual mean (based on seasonally variation) of physic-chemical attributes from RA and TN during the period 2014-2015.

Season Parameters	Stations	Summer		Monsoon		Winter		Annual mean	
		Mean	SD	Mean	SD	Mean	SD	Mean	SD
pH	RA	7.666667	0.15	7.70	0.10	7.70	0.10	7.69	0.11
	TN	7.566667	0.12	7.80	0.20	7.77	0.15	7.71	0.18
Water temperature	RA	33.66667	1.53	27.33	1.15	26.00	1.00	29.00	3.71
	TN	35	1.00	28.67	0.58	28.00	1.00	30.56	3.43
Total rainfall	RA	46.33333	11.02	643.33	81.45	60.00	10.00	249.89	298.03
	TN	68	7.21	459.33	1.15	23.67	13.20	183.67	207.78
Dissolved Oxygen mg/L	RA	4.133333	0.06	4.42	0.01	4.53	0.01	4.36	0.18
	TN	4.54	0.03	2.95	0.01	3.32	0.01	3.61	0.72
BOD mg/L	RA	6.563333	0.01	13.91	0.01	8.22	0.01	9.56	3.34
	TN	25.06333	0.01	3.73	0.01	3.82	0.01	10.87	10.65
Chloride g L	RA	19.57667	0.01	20.67	0.06	18.36	0.01	19.53	1.00
	TN	22.42333	0.01	20.19	0.05	21.25	0.01	21.29	0.97
Nitrate μM/L	RA	76.12333	0.01	121.88	0.01	80.12	0.02	92.71	21.95
	TN	96.66333	0.01	112.46	0.01	124.59	0.55	111.24	12.13
Ammonia μM/L	RA	99.65667	0.01	91.14	0.01	75.67	0.06	88.82	10.53
	TN	142.8333	0.01	105.93	0.46	149.37	0.06	132.71	20.28
Total Phosphorus μM/L	RA	0.386667	0.01	0.34	0.01	0.32	0.01	0.35	0.03
	TN	0.816667	0.01	0.85	0.01	0.52	0.01	0.73	0.16
Sulphate mg/L	RA	226.7367	0.01	215.43	235.85	231.77	0.58	224.65	7.26
	TN	276.8267	0.01	235.84	0.01	281.47	0.02	264	21.74
Calcium mg/L	RA	367.3333	0.01	401.74	0.02	378.34	0.01	382.47	15.22
	TN	508.6333	0.06	481.24	0.01	464.56	0.01	484.81	19.27
Magnesium mg/L	RA	135.6167	0.01	120.78	0.58	136.95	1.15	131.11	7.80
	TN	167.4267	0.01	164.52	0.01	149.33	0.01	160.43	8.42



a.

b.



**Figure 2 (a-f) Pearson's correlation of correlogram between physico-chemical parameters in southeast coastal of India from 2014 to 2015.**

Correlation significant at  $p < 0.05$ .

Abbreviations: pH, WT: Water temperature, TP: Total phosphorus, Nit: Nitrate, Do: Dissolved oxygen, BOD: Biological oxygen Demand, Cl: Chloride, AM: Ammonia, Ca: Calcium, Mg: Magnesium, Rf: Rain fall, SP: Sulphate.

### Correlogram analysis between physico-chemical parameters determined

The relationship between different physico-chemical concentrations were analyzed by Pearson's correlation coefficient. The correlation analysis is a bivariate method which is applied to describe the relation between two different parameters. The high correlation coefficient (near +1 or -1) means a good relation between two variables, and its concentration around zero means no relationship between them at a significant level of 0.05% level, it can be strongly correlated, if  $r > 1$ , whereas  $r$  values between 0.5 to 0.7 show moderate correlation between two different parameters. In RA during summer season was positively correlated with total phytoplankton density related to Ca, SP, TP, Cl, AM in strongly negatively correlation with Mg, Nit, DO, BOD. In TN during Total phytoplankton density were strongly positively correlation at summer season Mg, TP, DO, Nit in strongly negatively correlated with WT, Ca, AM, Cl, RF, BOD.

In RA during monsoon total phytoplankton density was positively correlated with Mg, SP, TP, AM, Nit, WT, Cl and negatively correlated with DO, pH, Ca. Whereas in TN positively correlated with WT, RF and moderately correlated during monsoon season with Ca, TP, AM, Nit, BOD, Cl. Total density phytoplankton in RA during winter season was positively correlated with Mg, AM, Ca and negatively correlated with RF, pH, BOD. Related kind of rainfall data was described by (Saravanakumar et al., 2008) from mangroves of Kachchh-Gujarat.

Whereas in TN positively correlated with pH, WT, Nit, DO and also moderately correlation with Cl, BOD, AM, TP, SP, Ca, Mg and negatively correlation with RF at winter seasons. The results of the present study in agreement with the earlier workers described by (Sundaramanickam et al., 2008; Santhosh Kumar and Ashok Prabu, 2014). A related statement has been

completed from other coastal waters of India (Madhupratap et al., 2001; Prasannakumar et al., 2002 and Sarma, 2006) (Figure 2 a-f)

### Principal Component Analysis (PCA)

Principal component analysis was conceded out to extract the most significant factors and physicochemical parameters affecting the water quality and phytoplankton density. Due to the complex relationships, it was difficult to draw clear conclusions. However, not only could principal component analysis extract the evidence to some extent and explain the structure of the data in detail, on temporal characteristics by clustering the samples, but it could also describe their different characteristics and help to elucidate the relationship between different variables by the variable lines. Based on the 13 physicochemical parameters were reduced to 2 main factors (factors 1 and 2) from during temporal variables RA and TN at south east coastal India, Tamil Nadu.

In RA was component 1 to the % total variance (54.23%) and component 2 (39.03). A correlation matrix positively loading of the variables was computed to axis 1 were represented to WT (0.3495), TP (0.2815), SP (0.9509), Mg (0.9937) during at summer season. Phosphorus is an vital nutrient and can play an important role of limiting factor (Dugan 1972). It is responsible for the growth of the phytoplanktons in aquatic ecosystems (Hutchinson 1975). According to the Pollution Control Board (1998), allowable limit of phosphate phosphorus for the discharge into inland surface water is  $5 \text{ mg L}^{-1}$ . The higher sulphate concentration is a characteristic of brackish water (Asonye et al. 2007), which supports the results of this study and negatively loading of the parameters in axis 1 were represented by pH (-0.1035), DO (-0.2552), BOD (-0.9772), Cl (-0.8454), Nit (-0.99666), Am (-0.1600), Ca (-0.9506) negatively loading with component 2 WT (-0.9195), Cl (-0.5279), Am (-0.09799), TP (-0.9535). And also to positively loading axis 2 were represented to pH (0.2248), RF (0.0197), DO (0.9608), BOD (0.2102), Nit (0.0755), SP (0.3006), Ca (0.3082), Mg (0.0746) during at winter season. The minor pH makes the nutrients (such as phosphate and nitrate) available to the primary producers (Davies et al. 2009). And monsoon and negatively loading WT (-0.9195), Cl (-0.5279), Am (-0.9799), TP (-0.9535), (Fig.3)(Table 2). The most important sources of chloride in the natural waters are sediments (Mishra et al., 2008).

In TN was component 1 to the % total variance (53.95%) and component 2 (42.04%). A correlation matrix positively loading of the variables was computed to axis 1 were represented to pH (0.6366), RF (0.2748), Nit (0.9550) at monsoon season. Nitrate in water bodies is liable for the growth of the cyanophycean and chlorophycean algae (Abdul, 1998). And negatively loading WT (-0.9730), DO (-0.9275), BOD (-0.9862), Cl (-0.7990), Am (-0.2301), TP (-0.5443), SP (-0.2754), Ca (-0.9714), Mg (-0.7332) at summer. The biological oxygen demand (BOD) is of most importance in the pollution monitoring. It is an approximate measure of the amount of the biochemically degradable organic matter present in the water and is used mainly to determine the degree of pollution in the water bodies, their self-purification capacity and the pollution stress of the wastewaters (Mishra et al., 2008; Rai and Tripathi, 2008). And also axis 2 were represented to positively loading variables in WT (0.06821), DO (0.3715), BOD (0.1592), Cl (0.6043), Nit (0.2874), Am (0.9741), SP (0.9623) at summer and winter season. Negatively loading to variables in pH (-0.1908), RF (-0.9615), TP (-0.8348), Ca (-0.2257), Mg (-0.6749) at summer and monsoon (Fig. 4) (Table.2). This could be due to larger production of sea salt aerosol because of the strong winds prevailing over the northwestern Indian Ocean, particularly during the southwest monsoons (Johansen et al., 1999).

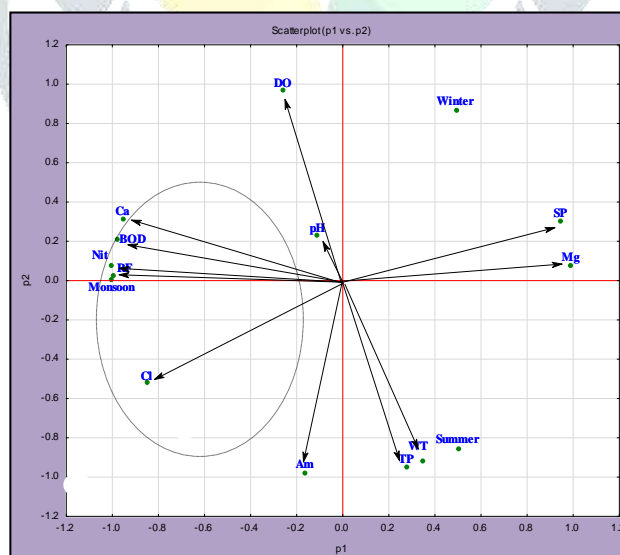


Figure 3. Biplot diagram of PCA analysis summarizing the contribution of dominant physicochemical factors in different season at RA

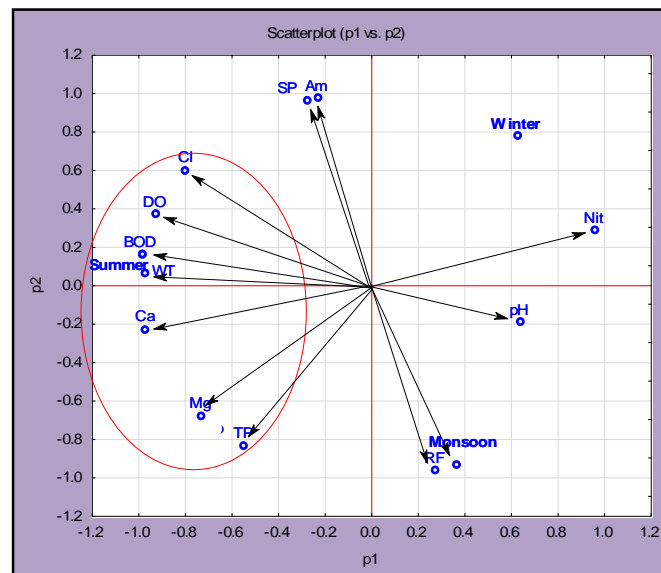


Figure 4. Biplot diagram of PCA analysis summarizing the contribution of dominant physicochemical factors in different season at TN

Table 2. Principal component analysis (PCA) of physico-chemical parameters in the RA and TN during year 2014 to 2015.

Variable	Rameswaram(RA)		Tuticorin(TN)	
	Component 1	Component 2	Component 1	Component 2
pH	-0.103567	0.224882	0.636663	-0.190841
WT	0.349526	-0.919535	-0.973083	0.068218
RF	-0.992475	0.019706	0.274863	-0.961577
DO	-0.255266	0.960844	-0.927561	0.371529
BOD	-0.977234	0.210204	-0.986281	0.159264
Cl	-0.845482	-0.527959	-0.799089	0.604358
Nit	-0.996668	0.075525	0.955039	0.287404
Am	-0.160042	-0.979945	-0.230133	0.974190
TP	0.281526	-0.953581	-0.544338	-0.834806
SP	0.950996	0.300625	-0.275407	0.962341
Ca	-0.950689	0.308279	-0.971421	-0.225708
Mg	0.993732	0.074654	-0.733249	-0.674909
Summer	0.503936	-0.858611	-0.986816	0.155643
Monsoon	-0.999406	-0.002836	0.362951	-0.933143
Winter	0.495470	0.861447	0.623865	0.777500
Eigenvalues	8.6781	6.2460	8.6323	6.7276
% Total variance	54.2381	39.03	53.9522	42.0477

**CONCLUSION**

This paper summarizes the seasonal variations of physic-chemical parameters of Rameswaram (RA) and Tuticorin (TN) with an exploration statistical data output. RA site was less polluted with high diversity of phytoplankton. However TN site was influenced by maximum disturbances reflected in terms of high values of pH, RF, Nit, low values of WT, DO, BOD, Cl, Am, TP, SP, Ca and minimum density of phytoplankton. The overall study provides a baseline data on the prevailing condition of the of Tuticorin (TN) comparing to Rameswaram (RA).

**CONFLICT OF INTEREST**

We declare that we have no conflict of interest.

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