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Environment International 32 (2006) 174-179



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Factor analysis of water quality characteristics including trace metal speciation in the coastal environmental system of Chennai Ennore

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Available online 7 October 2005

Abstract

Statistical analysis of water quality parameters including trace metal speciation was undertaken with a view to seeing the interrelationship between different variables and also to identify probable source components in order to explain the pollution status of Chennai Ennore coastal environmental system. Factor analysis has been used in the present work. This is essentially a data reduction technique and will suggest how many variates are important to explain the observed variances in the data. The possible variances in the water quality parameters may be due to either sources of anthropogenic origin or natural variances due to the season or due to different biogeochemical processes that are taking place in the system. When this analysis was carried out with our data on water quality parameters in the above coastal environmental system, we found that the prominent factor or the first factor called the eutrophication factor explained 24.51% of the total variance (comprised of variables like DO, pH, SS, ammonia-N, phosphate and silicate). The second factor called the copper contamination factor explained 10.61% (comprised of variables like labile Cu, total Cu and particulate Cu) and the third factor called metal removal factor explained 10.11% (comprised of variables like particulate Zn, particulate Pb and water temperature) of the variances, respectively. Although there are four more factors, they are all having variances less than 10%. From this study, it is seen that eutrophication is the main source component of pollution to the surface waters of this estuary and its adjacent coastal waters compared to dissolved trace metals.

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Keywords: Statistical analysis; Factor analysis; Water quality; Eutrophication and trace metal speciation

1. Introduction

To understand the effect of land-based effluents on coastal eco-systems, environmental authorities have been promoting a large number of monitoring campaigns in which data on many variables are collected over wide areas for extended periods. The voluminous amount of the data generated in such research programs needs to be rationalized by the application of statistical methods such as multivariate techniques, which include factor analysis and principal component analysis.

The present work discusses the results obtained in a detailed research program on the metal ion speciation studies in coastal environmental system of Chennai Ennore.

2. Description of study area

Ennore estuary is situated towards the North of Chennai harbour and facing the sea in the east (Fig. 1). It is surrounded by the Manali industrial complex and joined by the Buckingham canal. In addition, Korattaliyar River, red hills surplus canal and Kosasthaliyar River join the estuary from the western end. These water bodies discharge treated/untreated industrial effluents, urban sewage, thermal effluents (from the nearby thermal power stations), etc. through Ennore estuary to the nearby Ennore coast. This estuary is hence expected to contain elevated levels of both trace metals and dissolved organic matter relative to the open sea environment.

3. Sampling design

The sampling was carried out during the period May 98 to December 2000 along Ennore transect consisting of three stations inside the estuary (using fiberglass boat) and three

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Fig. 1. Sampling locations for Ennore estuary transect.

stations towards the seaside (using CRV 'Sagar Purvi') (Fig. 1). Due to logistics, one sampling was carried out on a particular month of every season summer (May), pre-monsoon (September) and monsoon (December). The season is with respect to the Northeast monsoon as Tamil Nadu gets the bulk of the rainfall in this season.



Fig. 2. Boxplot of water quality parameters along Chennai Ennore transect.

The surface water samples were collected using a precleaned and acid-washed bucket. The water samples for nutrients were collected in HDPE bottles and stored in ice and brought to the shore laboratory for further analysis. However, the coastal water samples were analyzed for nutrients on the site itself. The surface water samples for trace metals were collected separately in a pre-cleaned acid-washed polythene container. The differential pulse anodic stripping voltammetry (DPASV) was used to determine the concentration of trace metals like Zn, Pb and Cu in both dissolved phase and suspended particulate phase. The speciation of these trace metals was restricted to labile and non-labile discrimination.

4. Experimental

The analysis of different water quality parameters like dissolved oxygen (DO), water temperature, pH, salinity, suspended solids, nutrients like ammonia, nitrite, nitrate, phosphate and silicate were determined as given in standard methods (Eaton et al., 1999). The DPASV measurements were carried out with computer-controlled EG&G PAR Electrochemical system (Model 273A) and SMDE (Model 303A) setup within 1 month from the sample collection period. The whole SMDE setup including the stirrer was kept in a horizontal laminar flow air system (Atlantis, Pune). For the determination of total dissolved metals, the filtered seawater samples were irradiated with 1000 W UV light (UV Oxidation unit, Model HAPR-HP1000, HEBER, Chennai) in acidcleaned, Milli-Q water rinsed and dried quartz tubes in the presence of H₂O₂ for 5 h to remove dissolved organic ligands (Batley and Florence, 1986). Standard addition method and DPASV were used to determine the concentrations of total dissolved metals. The metals of interest (Zn, Pb and Cu) were first deposited on the medium-size drop of Hg under stirred condition from the HMDE setup at -1.2 V (vs. Ag/AgCl, saturated KCl) after removing oxygen from the solution by

purging high pure nitrogen for 5 min (Kuppusamy, 2002). After deposition, the stirring was automatically stopped and equilibrated for 15 s. During stripping, the potential was changed from -1.2 V to 0 V at a scan rate of 5 mV s⁻¹ with a pulse amplitude of 50 mV. The stripping peaks for these metals occurred around -1.1 V (Zn), -0.5 V (Pb) and -0.1 V (Cu). The linearity of calibration curve by DPASV was separately tested using aqueous metal standards (E. Merck) after suitable dilutions. The analysis of the labile metal was then carried out at a natural pH of the sample by DPASV but without UV-irradiation of the sample. The difference in concentration between the total dissolved and labile metals corresponded to the non-labile metals.

The suspended particulate matter collected on the filter paper during filtration was dried at 80 °C. The suspended particulate matter-bound trace metals were analyzed by DPASV following the procedure of De Luca Rebello et al. (1986).

5. Results and discussion

5.1. Factor analysis

The data so obtained for various water quality parameters including the total dissolved trace metal, labile metal and particulate bound trace metals (19 variables) were organized in a matrix with variables as columns and the samples (48 cases) as rows. SPSS version 9.05 software was used for carrying out the statistical analysis of the data after performing autoscaling for various parameters. Elimination of missing values (7 cases) led to the identification of 41 valid samples.

Principal component analysis was carried out to extract the various factors. The univariate statistics are represented as a boxplot (Fig. 2a and b). The Scree plot is shown in Fig. 3, which also includes the percentage variances explained by each component and gives an idea on how the different principal components were extracted. The eigenvalues for different factors, percentage variance accounted, cumulative percentage variance and component loadings (unrotated and Varimax rotated) are given in Table 1. Eigenvalues



Fig. 3. Scree plot of eigenvalues vs. components along with percentage variances vs. components for Ennore estuary transect.

Attacted values of valious factor analysis parameters for the Ennote estuary transect												
•	Tot	tal variance explained Before rotation	> <	Total variance explained After rotation								
Component	Extraction sums of squared loadings			Rotation sums of squared loadings Eigen-values								
								Total	% of variance	Cumulative %	Total	% of variance
	1	4.849	25.520	25.520	4.657	24.512	24.512					
2	2.642	13.903	39.422	2.016	10.612	35.124						
3	2.140	11.263	50.686	1.921	10.108	45.232						
4	1.522	8.009	58.694	1.865	9.815	55.047						
5	1.462	7.693	66.387	1.703	8.961	64.008						
6	1.249	6.575	72.962	1.460	7.683	71.690						
7	1.013	5.331	78.294	1.255	6.604	78.294						

Extracted values of various factor analysis parameters for the Ennore estuary transect

Extraction method: principal component analysis.

Table 1

greater than 1 were taken as criterion for the extraction of the principal components required for explaining the sources of variances in the data. The objective of this analysis was primarily to create an entirely new set of variates or factors much smaller in number compared to the original data set of variables for inclusion in subsequent analysis.

From the descriptive statistics (not represented here), it was seen that there were high standard deviations for certain water quality parameters, and these were the result of intense seasonal variations and also due to the influence of the tides on the physico-chemical characteristics of this transect. This, in turn, was the effect produced by the discharge of industrial effluents and sewage effluents from the nearby Manali industrial complex and the Buckingham canal. Such an explanation was also offered by Gonzalez-Mazo et al. (1998) who has done the work on identifying processes involved in the hydrochemistry and environmental quality of the Bay of Cadiz, Spain.

Table 1 shown above reflects the eigenvalues and variance percentages (accounted for and cumulative) corresponding to the principal components both before Varimax rotation and after Varimax rotation. The Varimax rotation was performed to secure increased principal components of chemical/environmental significance. This analysis resulted in the explanation of 78.3% of variances in the data. Many concentration distributions were very skewed, the exception being water temperature and pH.

The principal component analysis was actually performed on the correlation matrix between the different parameters followed by Varimax rotation and the same has been used to examine the association between them.

The parameter loading for the seven components from the principal component analysis of the data set are given in Table 2. It can be seen from this table that most of the variables associated with each factor are well defined and contribute very little to the other factors, which helps in the interpretation of results. The exceptions for this are the variables WT, pH, NIN, NN and total dissolved copper (CuT). Further, it can be inferred that the first factor (F1), which explains 24.512% of the total variance, is related to the variables DO, pH, suspended solids, ammonia-N (AN), inorganic reactive phosphate (IRP) and silicate (SIL). While the parameters DO and pH are negatively loaded with this factor, the nutrient parameters AN, IRP&SIL and SS are positively loaded with this factor. This factor may be termed as eutrophication factor because the sign of the loadings of the different parameters is consistent with the eutrophication process. Thus, the eutrophication process occurs mainly through high input of nutrients from river/land

runoff, and hence, we expect high positive loading of nutrients, high negative loadings of DO and pH. These facts establish that the major source of nutrients to the Ennore estuary and its adjoining coast is from the land runoff through Korattaliar and Kosasthaliyar rivers and also from Buckingham canal. In other words, it may be suggested that the eutrophication factor will be a more robust indicator of the status of this transect.

Factor 2 (F2), on the other hand, explains 10.612% of the total variance and is positively loaded with copper in its dissolved, labile and particulate state. While the loadings of labile and particulate copper are high in this factor compared to other factors, the total dissolved copper shows only slightly high loading in the second factor compared to the sixth factor. As copper is a less toxic metal and is loaded separately compared to other metals, this factor may be termed as copper contamination factor. The copper

Table 2

Results of the factor analysis for water quality parameters for Ennore estuary transect for the period May 1998 to December 2000

Rotated component matrix											
Parameters	s Components										
	1	2	3	4	5	6	7				
WT (1)	0.409	-0.356	-0.490	-0.144	0.250	0.366	-0.182				
SAL(2)	-0.240	-0.0177	-0.082	-0.054	-0.122	0.902	-0.022				
DO(3)	-0.862	-0.004	0.198	0.049	-0.173	0.084	-0.200				
PH(4)	-0.578	0.286	0.051	0.224	0.114	0.320	0.018				
SS(5)	0.869	-0.035	0.017	0.032	-0.235	-0.077	-0.182				
AN(6)	0.889	-0.029	-0.177	0.060	-0.126	-0.092	-0.047				
NIN(7)	0.224	0.159	0.416	-0.083	0.217	0.006	0.764				
NN(8)	-0.106	-0.269	-0.428	0.224	-0.252	-0.157	0.647				
IRP(9)	0.896	0.049	0.058	0.145	-0.131	0.010	-0.016				
Sil(10)	0.804	0.083	0.075	-0.035	-0.032	-0.178	0.279				
ZnL(11)	-0.170	-0.321	0.076	-0.028	0.817	-0.001	0.039				
ZnT(12)	-0.156	0.188	0.082	0.132	0.805	-0.152	0.004				
ZnP(13)	0.013	-0.104	0.791	-0.157	0.093	0.071	0.043				
CuL(14)	-0.113	0.763	-0.077	0.266	-0.054	-0.036	-0.208				
CuT(15)	0.232	0.589	-0.087	-0.196	0.204	-0.499	0.014				
CuP(16)	0.022	0.725	0.026	0.119	-0.071	0.036	0.130				
PbL(17)	0.372	0.292	0.022	0.805	0.027	0.123	0.012				
PbT(18)	-0.135	-0.091	0.002	0.925	0.072	-0.087	0.030				
PbP(19)	-0.148	-0.021	0.763	0.189	0.048	-0.126	0.009				

Extraction method: principal component analysis.

Rotation method: Varimax with Kaiser normalization.

A rotation converged in 31 iterations.



Fig. 4. Factor score for factor 1 for different samples along Chennai Ennore transect.

contamination into the Ennore estuary primarily arises by the industrial waste dumping from Manali industrial area, Buckingham canal discharges, agricultural irrigation systems through Korattaliyar rivers, etc.

Factor 3 (F3) explains 10.108% of the total varianace and is loaded with water temperature, particulate zinc and particulate lead. While water temperature is negatively loaded with this factor, that of the particulate zinc and particulate lead are positively loaded with this factor. This factor may be termed as metal removal factor. In effect, particles in suspension act as heavy-metal scavengers in the course of sedimentation, involving a series of chemical and physical processes including adsorption, the formation of complexes, ion exchange and inclusion within particles (Morales et al., 1999). An increase in the water temperature will disturb the contact between the metal ion and particulate matter, which removes the metal ion from the solution by the above-said processes. Thus, the sign of the loading of water temperature is consistent with the metal removal process by the suspended particulate matter present in the solution. Although we expect a good correlation between the suspended particulate matter and the metal concentration in the particulate matter, the correlation is very less in the present case.

Factor 4 (F4) explains 9.815% of the total variance and is loaded with labile lead and total dissolved lead. As lead is considered as a toxic metal and has origins from anthropogenic sources, we can term this as an anthropogenic factor. Both the parameters are loaded positively with this factor.

Factor 5 (F5) explains 8.961% of the total variance and is loaded positively with the parameters labile and total dissolved zinc. This factor may be termed as zinc contamination factor. It is further noted that zinc was not loaded heavily in the eutrophication factor requiring dealing with it separately.

Factor 6 (F6) explains 7.683% of the total variance and is positively loaded with salinity and negatively loaded with total dissolved copper. Such loading of salinity and total dissolved copper in a particular factor was also observed by Strain et al. (1999) during their work in the inlets around Nova Scotia. They attributed this type of association as an estuarine mixing factor. This they have decided because the copper was known to exhibit behaviour close to conservative similar to salinity. Hence, in the present case also, we can term this factor as estuarine mixing factor.

Factor 7 (F7), which accounts 6.604% of the total variance, is positively loaded with nitrite-N and nitrate-N. This factor may be termed as offshore forcing factor since nitrate concentration has been known to be controlled by large-scale processes (Strain et al., 1999).

6. Spatial relationship between the samples

An attempt was made to see the relationship between factor scores and the samples from various locations. The plot shown aside (Fig. 4) corresponds to the factor score of factor 1 for various samples. Here, sample nos. 1-6 corresponds to surface water samples along the six stations of the Chennai Ennore transect during May 1998 and 7-12 corresponds to the samples of same 6 stations but during December 1998. However, during 1999 and 2000, samples at these locations were collected in three seasons May, September and December, and hence, the remaining samples 13-48 correspond to that, respectively.

It may be seen from Fig. 4, during most of the period of 1998, that the stations show positive contribution to this eutrophication factor, whereas the same stations show negative contribution to this factor during the latter part of the period under study, viz. during 1999 and 2000. The stations that show dominant positive contribution correspond to first and last station along the coastal side of the Ennore transect during May 1998 and the first creek station during December 1998 and the second and third creek stations during May 1999 (summer). The higher positive contribution along the coastal waters during May 1998 may be primarily due to the nearby Ennore thermal power station fly-ash discharges. The higher positive contribution to the eutrophication factor in the creek may be due to the greater stagnation of the waters because of the existence of a sandbar near the mouth of the creek. A change-over from positive contribution to this eutrophication factor to negative contribution especially for the stations of this transect during latter part of 1999 and 2000 could be due to changes in the discharges along this creek. For example, during this period, dredging of the creek was carried out in addition to erecting a satellite port on the northern side of the creek. This could have altered the water quality, resulting in the observed negative influence to the eutrophication factor in this transect.

7. Conclusions

Based on the above discussions, it may be concluded that out of the 78.294% of variances explained by the seven factors, it is the eutrophication factor that explains most part of the observed variances in the data (26.512%). The parameters that are loaded in the factor include nutrients, pH, DO and suspended solids. The importance of trace metal pollution is taking a secondary role in the evaluation of pollution status of Ennore estuarine transect as they come in the second, third, fourth and fifth factors.

Acknowledgements

The authors thank Sri G. Govindarajan, SIC, CECRI, Madras Unit and Director, CECRI, Karaikudi and the Department of Ocean Development for their help in this work.

References

Batley GE, Florence TM. J Electroanal Chem 1986;72:121-6.

- De Luca Rebello A, Harkel W, Moreira I, Santelli R, Schroeder F. Mar Chem 1986:215–25.
- Eaton AD, Clesceri LS, Greenberg AE. Standard methods for examination of water and waste water, 19th ed; 1999. p. 3–39.
- Gonzalez-Mazo E, Forja Pajares JM, Gomez-Parra A. Trends Anal Chem 1998;17:58-69.
- Kuppusamy MR. Metal-ion speciation studies in coastal environmental systems of Chennai Ennore and Palar, Mahabalipuram PhD thesis, Madras University 2002 (July); Chapter IV: 112–129.
- Morales MM, Marti P, Llopies A, Campos L, Sagrado S. Anal Chim Acta 1999;394:109-17.
- Strain PM, Yeats PA, Mar Pollut Bull 1999;38:1163-70.