Chapter 5

Modeling of chemical parameters in the CES

5.1 Introduction

The present structure and behavior patterns of estuaries are a result of the various biogeo and physicochemical processes. The level of complexity of the system depends on the number of interacting or superimposed processes and increases generally with time. The knowledge on the dynamics of evolution and the present state of affairs is essential for the development of a working model. Models should not only explain the experimental data but should predict future probability. This is an attempt to predict the overall reactivity of the Cochin Estuarine System in terms of the behaviour of boron.

The estuarine systems are having a special significance in the hydrosphere because of its role as a link between land and sea. The impact of human activities is at its maximum in the estuarine waters. The agricultural drains, industrial effluents sewage and sullage etc deliver considerably to this system modifying the chemical characteristics. Compared to the rivers and oceans, the estuarine waters are the most vulnerable points in terms of pollution. A special significance is attributed in the hydrosphere to the estuarine systems because of the multitude and complexity of the processes; the system can not be defined by interpreting any of the individual properties. The various independent but interdependent processes include geochemical processes such as sedimentation, resuspension, precipitation and dissolution, chemical transformation such as complexation, exchange, species modification etc, and biochemical process such as uptake, depuration, death and decay. The seawater undergoes various chemical and physical modifications during its mixing with fresh water from the land. The dilution of seawater, which is the major phenomena during mixing, is associated with a re speciation of the elements present in these waters also. The speciation and residence time of any species in an estuary is dependent on fresh water discharge, density gradients, atmospheric input, tidal and water current pattern. No comprehensive model is available which can be applied to an estuarine system in its totality.

The various approaches adopted for the interpretation of estuarine system can be grouped in to two and primarily utilises only the physical parameters. In the first group the averaging of tidal flow (Tee, 1976; Sinha *et al.,* 1995, Sinha *et al.* 1998; Prandle, 1978) and in the second group time averaged equations of motions (Nihoul and Ronday, 1987) were used. A few theoretical models using the baraclinic effects are also available (Smith and Chang, 1987; Jin and Raney, 1991). The model developed in this study, though considers both tidal contribution and time averaged flow, and basically is different from these two. In the first phase, because of the regular and continuous pattern of the physical and chemical processes, the system is considered to be at a steady state and so the initial state will not have much significance in defining the system. Secondly chemical reactivity of the estuary is assumed to regulate the species concentration of any element in the system than the physical processes. Thirdly, in positive estuarine system like CES, where regulate flow of fresh water and tidal intrusion of sea water are present, the mixing time and the flushing time can be considered as better representative of the physical processes rather than the tidal flow.

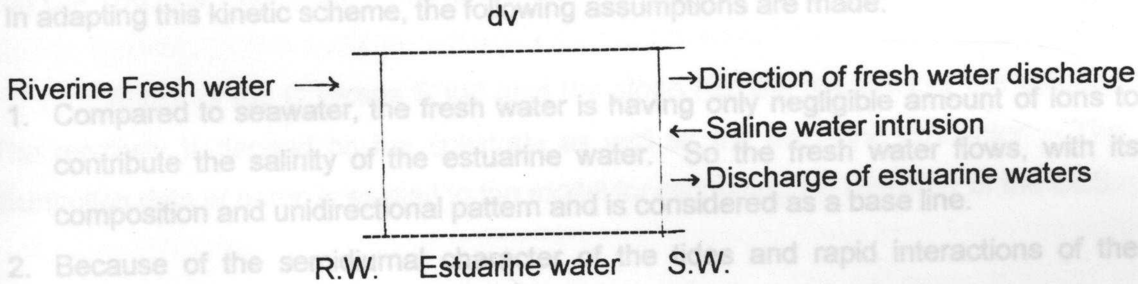
5.2 The System

1. As mentioned in earlier chapters, the CES is a tropical positive estuarine system with two distinct arms through the rivers Periyar at the North and Muvattupuzha at the South. These rivers which flows through the adjoining land masses of agriculture, are the major contributors of fresh water to the system and so contains considerable vegetative matter.
2. The Barmouth, ca 450m wide, is the only permanent opening to the sea.
3. The average depth of the estuary is around 3m and the maximum tidal height is about 1m. The tidal processes thus have profound influence in this system.

4. During monsoon months, the river and estuary get flooded with fresh water and will show only fresh water characteristics.
5. During postmonsoon and premonsoon the riverine flow is considerably slow and the estuarine system up to the river mouths will give saline characteristics.
6. Though the system is highly positive with a flushing time of 7 days and the depths are very low, significant vertical salinity gradient is observed in the entire estuarine region.
7. Though the average depth is very low, the high organic content in the sediments results in an anoxic condition in the sediments.

5.3 The Model

The estuarine system with its riverine discharge and saline water intrusion can be considered in a broader sense a flow reactor.



The reactor start from the river mouth where salinity is zero or near to zero and ends at the Barmouth where salinity is equivalent to the salinity of seawater. Through the reactor the reactant 1, the fresh water, flows at a flow rate of V m/s. The reactant 2, the seawater, enters the reactor at a velocity that can be indicated by the time average of high tide and leaves the reactor by the time average of low tide.

If U liter/ S is considered as the rate of flow of the chemical entity to the reactor and C the concentration of the entity, then during a time interval dt the amount of the species that is transferred to the reactor will be UC dt. If the order of the reaction in the rate transformation

$V = -dc/dt = k C^n$.

If dv is the volume of the reactor of reaction that will take place in a time interval dt, the rate $v = -dc/dt = kc^n dv$.

After a period of time the component leaves the compartment at the rate of U (C + dc)dt. Because of the regular cycling feature, the reactor is assumed to be in a steady state: or the rate of addition and the rate of removal are equal.

The steady state contains contributions from

(1) the amount of species that enters the reactor, i.e., U C dt.

(2) the amount of species that leaves the compartment i.e., U (C+dc) dt.

(3) the amount of species that undergoes reaction i.e., k C^n dv dt.

At the steady state UC dt = U (C+dc) dt + kC^n dv dt.

Rearranging -U dc dt = kC^n dv dt

or dc/C^n = -k dv/U

In adapting this kinetic scheme, the following assumptions are made:

1. Compared to seawater, the fresh water is having only negligible amount of ions to contribute the salinity of the estuarine water. So the fresh water flows, with its composition and unidirectional pattern and is considered as a base line.
2. Because of the semidiurnal character of the tides and rapid interactions of the chemical entities, the biochemical removal of any entity is considered to be not affecting the chemical environment of the system.
3. The sedimentary incorporation and exchange is regarded as the major phenomena in the regulation of availability of a particular species of the element in the estuarine waters. Considering the concentration changes associated with the mixing processes and possible magnitude of the unidentifiable interdependent multitude of the various transformations, the overall order of the reaction is considered to be one.
4. The tidal distribution of salinity is more or less regularised by the riverine flow and can be considered as in a steady state. The horizontal salinity gradient is a function of the ratio of flow rate to tide height.
5. The major ions, which constitute the salinity because of its conservative character generally, will exhibit a normalised distribution pattern with the addition of fresh water.
6. In a natural estuarine system, though the river flow can be measured precisely, the salinity intrusion, or the seawater influx, can not be measured. At the same time, the dilution patterns can be taken as an index of the rate of flow of seawater to the

estuary or from the estuary. As mixing will lead to a general dilution pattern, the volume element can be replaced by the salinity element.

7. Boron is a major element, which is conservative in seawater, but susceptible to biogeochemical modifications. So a comparison of the dilution patterns of boron with salinity can give an idea on the biogeochemical reactivity of the system.

The equation with this modification takes the form

$dC/C = - Kds/T$ where ds is the salinity element and T time averaged tidal height during the addition of seawater. T can be considered as a function of the physical processes operating in the system and K the geochemical reactivity. The ratio K/T can be considered as an index of the total estuarine reactivity that varies with changes on the physical ~~characteristics~~ processes and is ~~a~~ constant at a particular period.

This on integration

$\log C = - (K/T)\, S + \text{constant.} = - Ke\, S + \text{Constant}$

A plot of log C versus S will give the slope Ke, the reactivity of the estuary. The reactivity is depend on the substrate as well as the estuarine character. The distribution data of boron is applied to the model for estimating the reactivity of the CES.

5.4 Boron

Boron is one of the most important elements, which is significantly involved in the marine biogeochemical cycle. Boron, a metalloid, occurs in more than 100 minerals, the most common being tourmalins, a complex silicate mineral present in igneous rocks and sedimentary rocks. Boron in this form is largely inert and is released in to the environment at an extremely slow rate through natural weathering processes. The building block for the borates is BO_3 triangles linked together with Na or Ca ions. Natural weathering releases approximately 360×10^3 metric tons of elemental boron worldwide every year (Westall & Stumm ~~et al.~~, 1980). Although the amount of boron mobilised annually from anthropogenic sources has not been accurately determined, it is widely assumed that the most important source to surface waters are sewage, sewage sludge, and user industries such as detergent manufactures.

About 76 % of the total boron are present as boric acid, $B(OH)_3$, about 13% as borate, $B(OH)_{4^-}$ and nearly 11% is complexed with cations (Na, Mg, Ca, Co, Ni, Pb etc.)

(Robert R. Bryne, (Jr) *et al.,* 1974). Polysaccharides and high molecular weight polyhydroxy compounds complex with boric acid to form macromolecular structure (Deuel & Nuekom., 1949).

Boron is one of the major elements that have long been regarded as characterising the seawater and marine sediments. Soon after the fundamental work by Goldschmidt and Peters (1932) on the geochemistry of boron, an attempt was made to classify using the boron content whether a sediment had been deposited in marine or lacustrine environment (saline or fresh water environment). Boron was used as a geochemical indicator of salinity and temperature of the depositional medium and there will be relation between the boron content in the water and boron content in the deposited (Harder, 1970).

The concept of constantancy of major ions becomes a misnomer when one considers an estuarine environment. The rapid response of the estuarine environment to the time dependent physico-chemical parameters such as land runoff, precipitation and evaporation, brings about changes in the behavior of most of the elements of these waters (Shirodkar & Anand., 1985; Rajagopal *et al.,* 1981; Liss & Pointon., 1973; Narvelkar., 1980;). Exchange of solid solution components under varying chlorinity conditions in estuaries often result in nonconservative behavior of several major ions which normally bear a constant ratio with chlorinity in oceanic waters. The behavior of boron in estuaries has been studied detailed by several workers and the results indicated that some estuaries it was conservative (Liddicoat *et al.,* 1983) while in many estuaries boron showed removal and addition processes (Shirodkar & Anand., 1985; Zingde et al., 1987 Rajagopal, et al., 1981; Liss & Pointon., 1973).

Although, boron is an essential micro nutrient, low levels of born in phytoplankton indicate that the uptake of boron may not be the primary factor responsible for lower boron levels at the surface. The global average of boron and chlorinity in river water is 0.013 mg/l and 0.01 respectively (Livingston, 1963). This gives a B/Cl of 1.3. The ratio observed for surface water however is not indicative of any increase due to riverine influence.

The interesting features that can be seen from the depth profiles are two maxima for the boron and the B/Cl between 50 and 200m, and 300 and 500 m. Chlorinity also shows a maxima in these regions. The first maxima are at about the thermal discontinuity layer and appear to be the result of accumulation of colloidal and particulate matter. This may also be influence by the Gulf water. The second maximum centered around 400m which lies in the region of maximum apparent oxygen utilisation (AOU) (Naqvi, 1978) and is possible due to combined effect of the higher boron in the oxygen minimum zone and the high boron level associated with the Red sea water flowing at its characteristic density level.

A fairly good correlation coefficient of -0.73 observed between the suspended solids and PAR (percentage addition or removal) in Purna estuary suggests the importance of suspended load in controlling the levels of dissolved boron. A more or less inverse relationship between PAR of boron and suspended solids is observed in Ambika estuary. Good correlation between PAR of boron and chlorinity in Purna and Auranga estuaries and similar pattern of boron removal at low chlorinities suggests that the ionic strength also play an important role in the behavior of boron in these estuaries. High and low B/Cl ratios with the highest ratio of 0.269 and the lowest 0.202 observed in the coastal waters of eastern Arabian sea (Shirodkar & Singbal ~~*et al.*~~, 1992) indicate addition as well as removal of boron along the coast. The percentage addition and removal of boron calculated by taking in to consideration the world average B/Cl ratio for sea water (Uppstrom, 1974) 0.232, gave an addition from 0.43 to 16% and removal from 0.43 to 11.6% in the coastal waters.

Boron content showed a high correlation with chlorinity in the Central West Coast of India (Shirodkar et al., 1982) at various depth stations, high average variations of B/Cl was reported at oxygen minima. In general lower values of boron in the upper layers of shallow stations show that boron is utilised by phytoplankton and also it may be due to evaporation loss (Sevenko, 1977). In the south-western Indian Ocean region of the southern ocean (Sugandhini Naik *et al.*, 1986). The average concentration of boron was 4.62 ± 0.44 mg/kg and the B/Cl ratio is 0.242 ± 0.023. The relation B (mg/kg)= 0.227 X Cl ± 0.050 with the observed mean chlorinity in this case as 19.124 gives boron concentration as 4.39 mg/kg and the corresponding B/Cl as 0.230. The ratio, as calculated, is somewhat as higher than that obtained from low chlorinity Baltic Sea water by Dyrssen and Uppstrom (1974), which was 0.230. Culkin (1965) has reported that the average concentration of boron to the 4.5 mg/kg at a salinity of 35‰.

It is well known that marine clay sediments are strongly enriched in boron (100 ppm), as they, together with altered oceanic crust, are the earth's most significant boron reservoirs (Goldschmidt, 1954; Thomson et al., 1970; Harder, 1974).

The water temperature, too, has an effect on the boron content (Harder, 1959b, 1961b). Sometimes the organic compounds influence the boron content of clays. Eager (1962), Curtis (1964) and Harder, (1970) have shown an inverse relation ship between boron content and organic carbon. It appears that the presence of organic matter and relatively low contents of total boron in these sediments (perhaps not in all) are related (Eager, 1962).

In an aquatic system, sediments store by removing it from the overlying water through the physical process of adsorption and chemical complexation. Boron from the overlying water is removed by the differential adsorption on to suspended solids during the estuarine mixing of sea and river waters (Levinson and Luddwick, 1976; Liss and Pointon, 1973). Biological removal of boron by phytoplankton have also been observed which adds boron back to the sediments on the death and decay of phytoplankton (Subba Rao, 1981; Shirodkar *et al.,* 1982).

Acid treatment was carried out for two calcareous sediments, to examine the influence of biogenic carbonates on the bulk content and isotopic composition of boron in these sediments. The sediments contain 58% and 36% of HCl soluble component (carbonate), and the residues corresponding to pelagic clay and diatom ooze respectively. Boron content of pelagic clays determined in this study (Tsuyoshi Ishikawa & Nakamura., 1993.) vary from 96 to 132 ppm, which is essentially consistent with the range of 80-157 ppm given in Spivack *et al.,* 1987 and 120 ppm for average argillaceous sediments (Harder, 1974).

5.5 Boron in CES - Results of the present study

Dissolved boron in the surface water of Cochin estuary varied between ND level to 3.07 mg/l (Annexure.5a). Boron in the northern zone of the estuary varied from ND level to 2.36 mg/l and in the southern zone 0.16 to 3.07 mg/l, the maximum value was showed in the Barmouth. Boron in the bottom water has slightly higher concentration than surface water. In the bottom water dissolved boron varies from ND level to 5.91

mg/l in the north zone and the maximum value was showed in station.1. In the south zone, dissolved boron concentration varied from 0.31 to 3.58mg/l.

Dissolved boron generally showed an increasing trend in surface waters during the three seasons from upstream to downstream except in station 1 during premonsoon and monsoon (fig: 5.1 a & Table 5.1). Station 1 showed high values during premonsoon and monsoon season compared to station 2, this may be due to the input from anthropogenic sources.

Table 5.1. Seasonal average of dissolved boron in water (ppm).

Station	1	2	3	4	5	6	7
Postmonsoon. S	0.38	0.69	0.95	1.79	1.92	1.23	0.49
B	2.16	0.75	1.05	2.11	2.80	1.14	1.32
Premonsoon. S	0.29	0.15	0.38	1.09	1.81	0.87	0.67
B	0.39	0.48	0.94	1.61	2.22	1.14	0.79
Monsoon. S	0.70	0.27	0.29	0.69	0.38	0.98	0.52
B	0.59	0.15	0.32	0.33	2.27	0.88	0.79

S - surface; B -bottom

The bottom water also showed a similar trend as that of surface water monsoon (fig: 5.1 b) in all stations except station 1 and station 7 during postmonsoon. In postmonsoon and monsoon, station 1 have higher values than station.2 and also in the southern zone station 7 showed higher values than station 6 in postmonsoon season. Generally boron in the surface and bottom waters of Cochin estuary increases with salinity, clearly indicating the introduction of boron in to the CES through saline water.

Water-soluble boron in the estuarine sediments of Cochin varied from 4.5 to 61.18 ppm in the northern zone and in the southern zone, the value varied from 2.43 to 103.42 ppm (Annexure 5 b). Water-soluble boron in the sediment showed maximum values in station 2 during premonsoon monsoon (fig: 5.1 c & Table 5.2). There was no significant seasonal trend for water-soluble boron in the Cochin estuarine sediment.

Table 5.2. Seasonal average of water soluble boron in sediment (ppm).

Station	1	2	3	4	5	6	7
Postmonsoon	13.11	14.59	12.16	23.01	16.02	12.94	16.74
Premonsoon	13.94	56.91	17.26	22.05	20.18	22.97	15.25
Monsoon	26.45	11.56	19.28	16.75	14.08	53.26	30.46

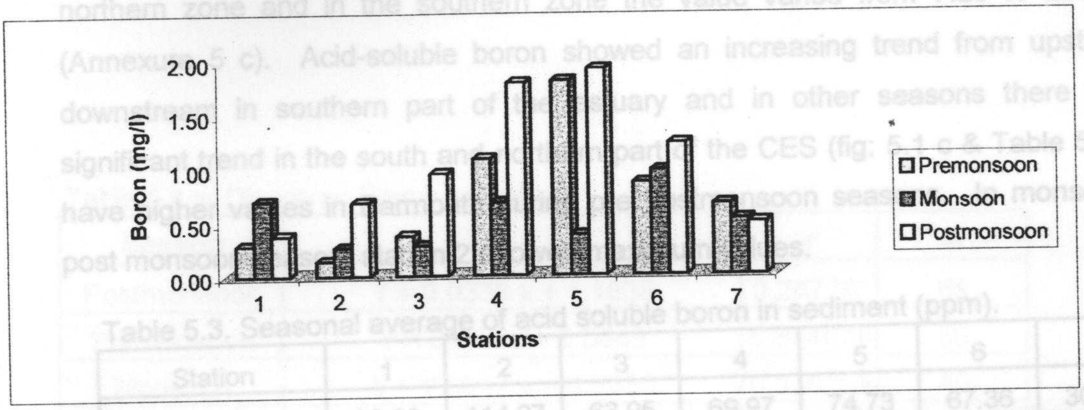


Fig: 5.1 a

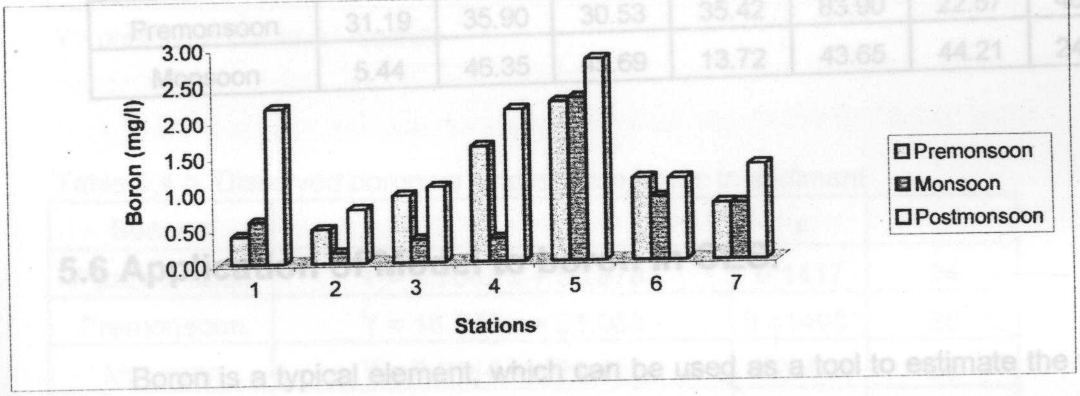


Fig: 5.1 b

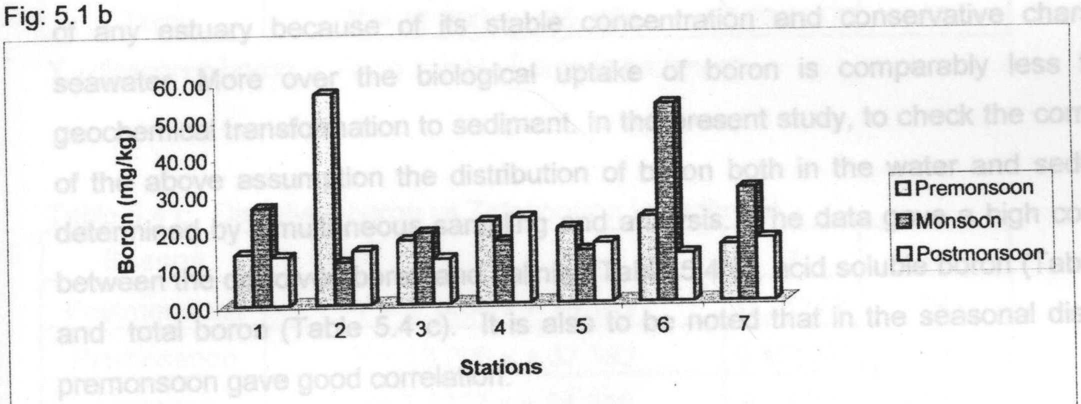


Fig: 5.1 c

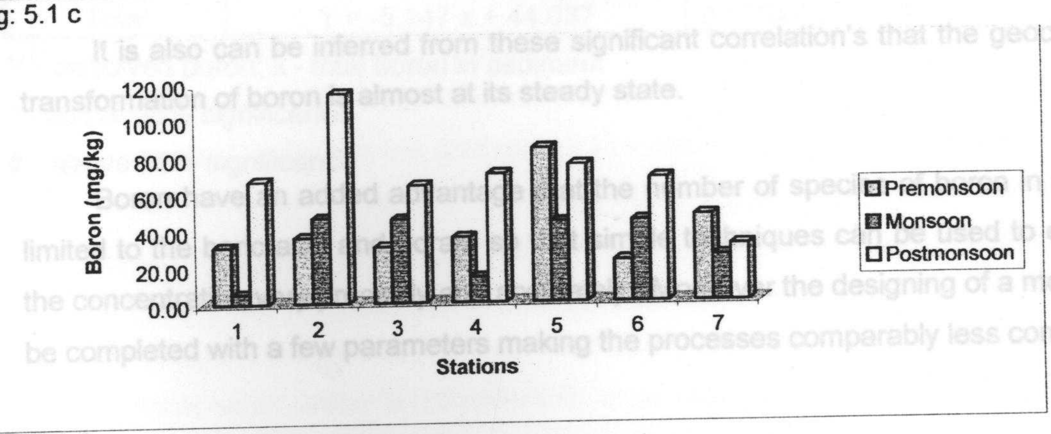


Fig: 5.1 d

Acid-soluble boron in the sediment varied from 5.42 to 191.54 ppm in the northern zone and in the southern zone the value varied from 7.26 to 220.5 ppm (Annexure 5 c). Acid-soluble boron showed an increasing trend from upstream to downstream in southern part of the estuary and in other seasons there was no significant trend in the south and northern part of the CES (fig: 5.1 c & Table 5.3), and have higher values in Barmouth during pre postmonsoon seasons. In monsoon and post monsoon season, station 2 showed maximum values.

Table 5.3. Seasonal average of acid soluble boron in sediment (ppm).

Station	1	2	3	4	5	6	7
Postmonsoon	66.63	114.27	63.95	69.97	74.73	67.36	30.55
Premonsoon	31.19	35.90	30.53	35.42	83.90	22.57	46.72
Monsoon	5.44	46.35	45.69	13.72	43.65	44.21	24.53

5.6 Application of Model to boron in CES.

Boron is a typical element, which can be used as a tool to estimate the reactivity of any estuary because of its stable concentration and conservative character in seawater. More over the biological uptake of boron is comparably less than its geochemical transformation to sediment. In the present study, to check the correctness of the above assumption the distribution of boron both in the water and sediment is determined by simultaneous sampling and analysis. The data gave a high correlation between the dissolved boron and salinity (Table 5.4 a), acid soluble boron (Table 5.4 b) and total boron (Table 5.4 c). It is also to be noted that in the seasonal distribution premonsoon gave good correlation.

It is also can be inferred from these significant correlation's that the geochemical transformation of boron is almost at its steady state.

Boron have an added advantage that the number of species of boron in water is limited to the boric acid and borate so that simple techniques can be used to estimate the concentration very precisely and accurately. Moreover the designing of a model can be completed with a few parameters making the processes comparably less complex.

Table 5.4 a. Dissolved Boron vs Salinity

Season		**r**	**n**
Postmonsoon	Y = 0.0339 x + 1.1038	0.28778*	68
Premonsoon	Y = 0.059 x + 0.0845	0.85407#	56
Monsoon	Y = 0.0617 x + 0.5395	0.53025#	40
Total	Y = 0.0403 x + 0.07	0.43944#	164

Y - dissolved boron, x - salinity

Table 5.4 b. Dissolved boron vs Acid-soluble boron in sediment

Season		**r**	**n**
Postmonsoon	Y = 6.7063 x + 58.978	0.1417	34
Premonsoon	Y = 18.352 x + 21.063	0.41405*	28
Monsoon	Y = 7.8144 x + 29.928	0.20526	20
Total	Y = 12.906 x + 35. 984	0.284117#	82

Y - dissolved boron, x - acid soluble boron in sediment

Table 5.4 c. Dissolved boron vs Total botron in sediment

Season		**r**	**n**
Postmonsoon	Y = 2.1454 x + 15.141	0.25242	34
Premonsoon	Y = 19.206 x + 37.392	0.40132*	28
Monsoon	Y= 7.9327 x + 54.919	0.13786	20
Total	Y = -5.147 x + 44.037	0.17042	79

Y - dissolved boron, x - total boron in sediment

* - above 95% significance

\# - above 99% significance

As the borate to boric acid ratio is part of an equilibrium coefficient, a definite relation between the total boron concentration and any one of the individual species will be present. In short, the reactivity, estimation methodology, the specious diversity and the concentration levels generally observed makes boron the most suitable element for modeling the reactivity of estuaries.

In this study, the observed concentration of boron is substituted to the flow reactor model. In the model C is replaced by the observed boron concentration and salinity (S) of that particular water mass. As the estuarine conditions during the three seasons, monsoon, premonsoon and postmonsoon are significantly different, the reactivity K is calculated independently for the three seasons. Also, the northern arm and the southern arm of the CES shows considerable variations in almost all of the estuarine properties, making it essential to apply the model separately to the two arms.

The relationship obtained and the correlation coefficient from regression analysis is given in table. 5. 5.

The analysis of the results obtained by substitution of data in the model indicate that

1) Except for monsoon season, the log C $_{(Boron)}$ exhibits highly significant correlation with salinity. This confirms the assumptions made during the development of the model. The dilution and flushing characteristics of the Barmouth of CES (coastal inlet) have been studied by many workers (Joseph and Kurup, 1989; Ajith Joseph, 1996). The major observations in these studies were that during the monsoon season, the Cochin inlet is subjected to considerable dilution. The monsoon season is characteristic for its (1) high flooding of the estuary with fresh water, (2) very low seawater intrusion and (3) very low flushing time. The geochemical reactivity as a result of the above reasons the estuary, during monsoon season will generally be very low and the observed concentration of any species of any element will have bearing only to the riverine discharge. The distribution studies of various chemical species done by earlier workers also confirm this (Lakshmanan *et al.,* 1982; Anirudhan, 1988; Babukkutty, 1991; Shibu, 1992; Vasudevan Nayar, 1992).
2) The order of reactivity from the K values are Monsoon> Postmonsoon> Premonsoon. As the flushing time is minimum during the monsoon season and as the fresh water inflow is considerably large blocking the seawater intrusion, the monsoon season will show the maximum K value. The absence of a significant

Table 5.5. Model parameters and correlation coefficient.

Log B vs Salinity

North		**K**	**r**	**n**
Postmonsoon	$\text{Log } C = 0.181025 S - 1.021343$	0.18103	0.354821*	34
Premonsoon	$\text{Log } C = 0.058261S - 0.883477$	0.05826	0.75147#	29
Monsoon	$\text{Log } C = -7.46826 S - 5.846901$	-7.46826	0.100168	22
Total	$\text{Log } C = 0.129865 S - 1.026544$	0.12987	0.435539#	89
South				
Postmonsoon	$\text{Log } C = 0.052425 S - 0.710616$	0.05243	0.699223#	30
Premonsoon	$\text{Log } C = 0.054386 S - 1.134497$	0.05439	0.820862#	23
Monsoon	$\text{Log } C = -0.116861 S - 0.492112$	-0.11686	0.044112	15
Total	$\text{Log } C = 0.053914 S - 0.766983$	0.05391	0.627226#	69

C - Boron, S - Salinity

Log MBAS vs Salinity

North		**K**	**r**	**n**
Postmonsoon	$\text{Log } C = -7.733952 S + 46.22119$	-7.73395	0.00263	38
Premonsoon	$\text{Log } C = 0.079815 S + 0.356413$	0.07982	0.449409*	31
Monsoon	$\text{Log } C = -5.521811 S + 2.029834$	-5.52188	0.329979	22
Total	$\text{Log } C= 0.493925 S - 1.508051$	0.49393	0.067384	93
South				
Postmonsoon	$\text{Log } C = 0.044282 S + 0.632511$	0.04428	0.463332*	30
Premonsoon	$\text{Log } C = 0.177233 S - 2.363043$	0.17723	0.15552	23
Monsoon	$\text{Log } C = 37.45318 S -42.6779$	37.4532	0.225078	15
Total	$\text{Log } C = 0.136258 S - 0.56832$	0.13626	0.139423	69

C - MBAS, S - Salinity

Log phenol vs Salinity

North		**K**	**r**	**n**
Postmonsoon	$\text{Log } C = -0.12006 S + 1.760073$	-0.12201	0.328424#	40
Premonsoon	$\text{Log } C = 0.268722 S - 1.905521$	0.26872	0.241558	31
Monsoon	$\text{Log } C = -10.2145 S + 2.720123$	-10.2145	0.081104	22
Total	$\text{Log } C = -0.326904 + 8.8666$	-0.3269	0.191943	96
South				
Postmonsoon	$\text{Log } C = -0.06367 S + 1.861709$	-0.06367	0.47172#	25
Premonsoon	$\text{Log } C = 0.137355 S - 1.870639$	0.13736	0.233575	22
Monsoon	$\text{Log } C = 0.008179 S + 11.811$	0.00818	0.245472	17
Total	$\text{Log } C = -0.79321 S + 2.057349$	-0.79321	0.30748#	64

C- Phenol, S - Salinity

* - above 95% significance, # - above 99% significance

correlation but indicates that the geochemical transformations are not the reason for these high K values. This can only be attributed to the irregular chemical character of the floodwater of monsoon.

3) In the postmonsoon, though have a reasonably low flushing time; the estuary gets sufficient time to reach the steady state. The reaction between the reactivity and the flushing time is more evident when we compare the postmonsoon with premonsoon. Though the concept of geochemical reactivity was not attributed to the seasonal variations in the distribution of various chemical species, such a relation between the postmonsoon and premonsoon was observed earlier also (Lakshmanan *et al.*, 1982; Anirudhan, 1988; Babukkutty, 1991; Shibu, 1992).
4) During the monsoon season, both the northern and southern regions exhibit more or less the same reactivity with respect to boron. The trend graphs give the same slope for both the regions. The prevailing of fresh water conditions, low salinity and fast flushing may be the reasons.
5) The reactivity coefficient K is greater in the northern region than the southern. The lower flow rate of river water and shallow nature of the water column may be the major contributors.

5.7 Application of the model to MBAS and Phenol.

The proposed model is applied to MBAS and phenol and the relation and correlation coefficients are given in Table. 5.5. In the case of phenol a significant correlation between log $C_{(Phenol)}$ and salinity was observed only for the postmonsoon season and the total period as a whole. The monsoon, as in the case of boron, showed the highest reactivity that can be attributed to the increased flushing (the decreased flushing time) and also to the insignificant addition of the seawater. The premonsoon, because of the higher flushing time, stagnant character of the water body and the high organic content shows only low geochemical reactivity as evidenced by a low value for K. The high retention time because of the low flushing during the premonsoon can lead to reactions other than geochemical such as photochemical reactions. The absence of any significant correlation between Log C and salinity during the premonsoon may be due to such side reactions. Also the insitu biochemical additions of phenols can contribute to the phenol concentration. Evidences for the photochemical transformations of phenols in aquatic systems are available in the literature (Polisois ~~et~~ ~~al.~~, 1975; Stephen Opsal & Benner.,1998).

The absence of significant correlation between log C $_{(MBAS)}$ with salinity indicates that MBAS is totally out of the model. The reason can be (1) the major source of MBAS in the aquatic system is anthropogenic so that the concentration of MBAS will have bearing only to the fresh water rather than the seawater. The basic structure of the geochemical reactivity model is the modification of chemical species brought to the estuarine waters from the seawater. The flow reactor considers the fresh water contribution to the concentration of chemical species as negligible or at a steady state. (2) MBAS belongs to a group of chemicals that are highly reactive, bioactive and biodegradable. The geochemical reactivity concept cannot be so applicable here; instead a model which can accommodate the above factors also to developed to explain the reactivity of MBAS. This requires more data on the reaction side of MBAS, which was beyond the scope of the present work. Work in this direction has already been initiated in this laboratory.

SUMMARY

Estuaries are unique environments that play an important role in the transfer of products of continental weathering to the ocean. Because of the major physico-chemical conditions existing in fresh and saline water, the distribution and chemical characteristics of constituents in dissolved and particulate forms get modified during the mixing processes in estuaries. Hence, assessment of the quality of water in an estuary is of great significance in the maintenance of a sustained ecosystem.

A wide spectrum of organic and inorganic compounds enters the estuary through different sources such as air, river and direct or indirect anthropogenic discharges etc. Since the subsequent behavior and fate of the substances depend on a variety of factors - physical, biological and chemical - the prediction of their behavior and fate is very difficult. Many pollutants adsorb on to suspended particulate material and get locked in the sediments on settling of these materials. Sedimentation of a pollutant may lead to serious long-term problems in an area, as resuspension of sediments and exchange with overlying water are regular process processes in estuarine dynamics.

Surface active agents are substances which cause lowering of the surface tension of liquids, particularly water. They can influence the structure and physico chemical properties of natural interfaces and mediate the processes of mass and energy transfer between different phases. They are involved in the processes such as bubble flotation of particles, microlayer enrichment and other surface effects. They are able to control the transfer of gases between the air-water interface

Surfactants (surface active agents and detergents) are very widely used as industrial and household cleaning agents, dispersants and emulsifiers. The number of these compounds is very large and it is continually increasing, although only relatively few types are in extensive use. Synthetic detergents have caused much concern due to their tendency, even in small amounts, to cause foam in rivers and at sewage plants. Harmful effects of detergents in natural waters may result from their general impact on the biogeochemical cycle of other pollutants and biogenic elements.

Natural surfactants from form a major part of the (estimated about 50-70%) marine humic substances. The fulvic acid fraction, one of the most important soluble component involved in the marine aerosol process, show the characteristics of wet surfactants. Coastal and estuarine waters in some densely populated areas receive significant quantities of various derived chemicals, which include anionic surfactants. These environments seem to be particularly sensitive to pollution with synthetic surfactants.

The CES is highly influenced by various anthropogenic activities like discharge of agricultural, industrial and urban wastes, operation of shipyard, oil and other transporting activities, fishing, dredging etc. A by-product of the dredging process is the resuspension of the bottom sediment, which contains stored toxic and other compounds. In the present study, the distribution and seasonal variation of anionic surfactants (MBAS), total phenols, chlorophenols and boron in the water and sediments of the CES has been studied

Seasonal values of MBAS showed high values in the surface water during monsoon compared to premonsoon and postmonsoon. In the surface water, MBAS showed a decreasing trend from upstream to downstream in the north zone during postmonsoon and in the bottom water an increasing trend towards downstream in premonsoon and postmonsoon in the southern part of the estuary. No significant trend was observed in the other seasons.

MBAS in the sediment showed an increasing trend towards downstream in the north zone. In the south zone a decreasing trend was observed during premonsoon. MBAS in the sediments of CES showed significantly high correlation with sedimentary organic carbon.

The seasonal values of phenolic compounds in the surface waters of Cochin estuary showed higher values in the northern part during monsoon and in the southern part during postmonsoon. In all the seasons, the average value of phenolic compounds in the surface waters of Cochin estuary along the Periyar River showed an increasing trend towards the upstream. This can be attributed to the input of phenolic compounds in to the estuary from anthropogenic or natural sources. The southern part of the estuary also showed a similar trend as that of the north zone, where phenolic concentration showed high values in the upstream station (Station no.7). Highest value for phenolic compounds during the monsoon months in the northern part of the estuary was in June 96 and in the southern part was in August 96. In the bottom water also, phenolic concentration showed an increasing trend towards upstream.

Postmonsoon in the northern part and premonsoon in the southern part showed to be exceptions to this. In postmonsoon months, very high values of phenolic concentration were observed during October 96 in all the stations. In premonsoon, May 96 showed maximum values in stations except barmouth. In monsoon season, all stations showed higher values except barmouth in all months. Localised high values were observed for phenols because of anthropogenic activities such as retting of coir, industrial discharge etc.

Phenolic compounds in the sediment during monsoon showed an increasing trend towards the downstream and in other seasons there was no specific trend and in the southern area station 7 showed maximum value in all seasons compared to station 6. The concentration of phenols in the sediment was always very low in stataion 1, except in November 96.

Chlorophenolic compounds are toxic to aquatic species, but to varying degrees depending on the number and the position of the chlorine substituents on the benzene ring. The chlorinated phenols consist of a group of 19 different isomers which include mono, di, tri, tetra and one pentachlorophenol. All these compounds are toxic to aquatic species, but in varying degrees with PCP being the most toxic. They are brought in to the environment, intentionally or unintentionally, through anthropogenic activities. The release of industrially derived halogenated organic compounds in to the aquatic environment is of great concern, mainly because of their toxicity, resistance to degradation, and tendency to bioaccumulate. Chlorophenolic compounds have been found to be the major constituents produced from lignin residues. Some of them are toxic and can get accumulated in living organisms.

The identification of the different chlorophenols in CES could be done with o, p and m chlorophenols because of the non availability of pure standards. The rest of the species observed in the G.C. is represented as fraction 1, 2 etc. The trends given denote decrease or increase, as the case may be, towards downstream.

In the Cochin estuary o-chlorophenol and p-chlorophenol showed low values in the surface water compared to bottom water in the northern part of the estuary and higher values in the surface water in the southern part. There was no significant trend for o-chlorophenol in the estuarine water. Seasonal average of o-chlorophenol showed high values during monsoon seasons in the surface and bottom water. In the sediment samples o-chlorophenol showed a decreasing trend during monsoon season and an increasing trend in the postmonsoon and premonsoon season in the northern part. No significant trend was observed in the southern part. In the sediment, p-chlorophenol showed a decreasing trend during monsoon in the northern part and in other seasons there was no significant trend in the north and southern part.

m-chlorophenol showed only a decreasing trend in the surface water during premonsoon and in other seasons the water and sediment samples had no significant trend in the study area. In water samples m-chlorophenol showed higher values during monsoon season in the surface and bottom water, but in sediment samples it showed low values during monsoon except in station.1. Generally m-chlorophenol showed higher values in the bottom water than surface water.

Fraction 1 showed a decreasing trend in bottom water in the northern part of the estuary during monsoon. The surface water of the south zone also showed a similar trend during monsoon and in other seasons the surface and bottom water had no significant trend. The sediment showed an increasing trend during monsoon in the northern and southern part of the study area.

Fraction.2 showed an increasing trend in the southern part during the premonsoon and a decreasing trend in postmonsoon seasons in the bottom water. The surface water and sediment samples had no significant trend in the two zones was observed.

Fraction.3 showed an increasing trend in the surface water of northern part during monsoon and postmonsoon. The bottom water also showed a similar trend during premonsoon of southern part. The sediment concentration showed no significant station wise trend. High values were observed in station.1 during monsoon.

Except for the increase in concentration during premonsoon of the southern part and a decrease during postmonsoon in the surface water of the northern part, no general trend was shown by fraction 4. The surface water concentration generally showed high values during premonsoon compared to bottom water where as in monsoon season the bottom water showed higher values. The sediment also showed a decreasing trend during premonsoon and monsoon in the southern part and monsoon in the northern part of the estuary. But in postmonsoon season, the southern part showed an increasing trend.

Fraction 5 showed high values in the surface and bottom water during premonsoon season in the northern part of the estuary except in station 1. Surface water of the northern part during premonsoon and postmonsoon showed an increasing trend. The southern part also showed an increasing trend during postmonsoon season. In the bottom water premonsoon showed an increasing trend in the north and in postmonsoon an increasing trend was showed in the southern part. The sediment in the north showed a decreasing trend during premonsoon and an increasing trend in postmonsoon. An increasing trend was observed in the south part during monsoon and a decreasing trend in premonsoon.

Fraction 6 showed generally higher values in the bottom water than surface in the northern part of the estuary where as in the southern part, surface water gave higher values except station 5. The surface water has showed an increasing trend in premonsoon and a decreasing trend in monsoon in the northern part. A decreasing trend was the observed in the bottom waters of the northern part in all seasons except station 4. In the northern part the sediment showed minimum during monsoon and maximum in postmonsoon season. In the sediment, the premonsoon values showed a decreasing trend in the northern and southern part of the CES and an increasing trend in southern part during postmonsoon.

Fraction 7 in the surface water showed low values during monsoon and in the sediment during postmonsoon. A decreasing trend was observed during postmonsoon and monsoon surface water in the southern part where as an increasing trend in the north during postmonsoon in the bottom water. Sediment samples showed an increasing trend in the southern part of the estuary during monsoon and in the north a decreasing trend during monsoon and postmonsoon.

A Kinetic flow reactor model is proposed to explain the overall reactivity of the estuary. The distribution data of boron was used to test the model. It was observed from the model that the order of reactivity was found to be Monsoon> Postmonsoon> Premonsoon. The absence of significant correlation between the model parameters in the monsoon season and the observed reactivity during monsoon was attributed to the irregular characteristics of the floodwater. The northern part was found to be more reactive than the southern part, may be due to the lower flow rate of river water and the shallow nature of the water column in the southern part. The model was found to explain the distribution pattern of phenol but MBAS was totally out of the model.

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Annexure - 2.1. Distribution of Salinity in the surface and bottom waters of Cochin Estuarine System (ppt).

Stations	Nov-95	Dec-95	Jan-96	Feb-96	Mar-96	Apr-96	May-96	Jun-96	Jul-96	Aug-96	Oct-96	Nov-96
1. S	ND*	0.12	0.08	5.21	1.24	0.08	0.06	0.10	0.06	0.06	0.02	0.03
B	ND*	0.12	0.64	7.69	10.42	0.11	0.15	0.1	0.07	0.06	0.02	0.04
2. S	0.08	2.01	0.20	6.47	1.27	0.31	0.24	0.14	0.07	0.07	0.03	0.04
B	0.07	7.22	4.41	14.05	12.84	0.93	0.4	0.1	0.07	0.07	0.02	0.04
3. S	1.16	11.13	11.86	5.79	4.51	1.21	11.77	0.22	0.07	0.07	0.02	0.02
B	1.22	14.59	15.43	17.83	17.69	1.52	13.09	0.22	0.7	0.07	0.02	0.02
4. S	18.57	14.33	14.44	22.59	19.30	8.12	23.75	2.65	0.10	0.13	0.24	17.63
B	18.66	20.39	18.36	30.39	29.71	15.06	25.05	2.82	0.1	0.12	0.024	27.6
5. S	29.53	23.29	29.62	30.50	33.44	25.00	24.65	2.42	ND*	3.08	2.10	31.75
B	30.43	23.77	30.93	32.72	33.75	34.24	33.57	2.94	ND*	32.51	19.65	32.15
6. S	3.06	11.67	13.75	13.87	21.94	17.29	17.41	0.34	0.11	0.22	0.07	13.58
B	3.34	16.8	18.09	18.11	26.45	18.22	17.41	0.53	0.11	0.6	0.07	15
7. S	1.14	10.67	15.78	12.31	18.32	7.12	12.28	0.19	0.08	0.21	0.05	5.27
B	1.36	12.27	18.64	13.4	20.23	9.05	13.02	0.19	0.1	0.31	0.05	6.76

S - Surface; B - Bottom ; ND* - Not Determined.

Annexure - 2.2. Distribution of dissolved oxygen in the surface and bottom waters of Cochin Estuarine System (ml/l).

Stations	Nov-95	Dec-95	Jan-96	Feb-96	Mar-96	Apr-96	May-96	Jun-96	Jul-96	Oct-96	Nov-96
1. S	ND*	3.71	3.43	3.3	3.06	3.67	4.17	4.79	5.46	4.05	4.33
B	ND*	3.8	3.77	3.43	2.45	3.92	4.49	5.42	5.06	4.03	4.3
2. S	3.68	3.51	3.43	3.3	3.67	3.67	5.14	4.45	5.09	4.91	3.65
B	4.66	3.73	3.23	3.55	3.06	1.71	4.75	4.88	4.9	4.59	4.02
3. S	4.08	3.9	3.13	2.94	3.75	2.82	5.32	4.66	4.55	3.68	2.98
B	2.81	3.04	2.79	2.57	3.43	3.3	4.37	4.58	4.63	3.95	3.22
4. S	3.86	2.38	2.94	3.06	3.67	2.82	3.76	3.71	4.17	3.26	2.98
B	2.74	3.04	2.45	2.82	3.79	2.94	2.99	3.83	4.19	3.68	2.98
5. S	2.91	2.95	3.33	3.92	4.29	2.45	2.9	4.44	ND*	3.28	3.31
B	3.68	4.09	3.72	3.55	3.79	3.18	2.54	3.46	ND*	2.54	3.46
6. S	2.66	4.18	3.72	3.67	2.94	2.69	3.53	5.54	4.54	2.6	2.89
B	3.41	4.18	2.64	2.45	2.94	2.45	3.25	4.92	3.57	2.53	3.01
7. S	3.95	3.33	2.64	3.55	2.57	2.69	1.99	3.22	2.75	2.15	2.06
B	2.71	2.95	2.45	3.06	2.45	1.96	3.13	3.1	3.83	2.98	2.79

S - Surface; B - Bottom ; ND* - Not Determined.

Annexure - 2.3.a. Distribution of sand (%) in the sediments of Cochin Estuarine System.

Stations	Nov-95	Dec-95	Jan-96	Feb-96	Mar-96	Apr-96	May-96	Jun-96	Jul-96	Aug-96	Oct-96	Nov-96
1	ND*	99.10	98.85	96.99	94.72	98.99	97.82	97.85	97.83	97.29	99.75	99.49
2	98.59	97.23	97.28	95.72	98.10	97.77	91.39	96.76	97.77	96.97	97.87	98.96
3	37.77	84.11	76.54	37.40	70.34	86.15	18.99	17.31	20.23	76.14	27.57	58.65
4	0.63	4.00	38.37	1.02	1.65	4.37	4.30	7.92	10.71	8.56	21.80	16.80
5	19.01	14.42	21.09	10.84	5.92	24.43	38.22	42.21	ND*	48.47	42.57	57.34
6	79.76	40.72	67.82	72.71	35.63	39.82	72.56	4.02	58.82	63.16	86.38	27.42
7	46.92	83.64	86.17	85.94	73.92	73.83	6.41	75.55	89.51	54.73	52.52	90.15

Annexure - 2.3.b. Distribution of silt (%) in the sediments of Cochin Estuarine System.

Stations	Nov-95	Dec-95	Jan-96	Feb-96	Mar-96	Apr-96	May-96	Jun-96	Jul-96	Aug-96	Oct-96	Nov-96
1	ND*	0.52	0.11	2.91	4.79	0.56	0.89	0.90	0.19	0.26	0.15	0.01
2	1.01	0.71	0.44	3.78	0.71	1.93	6.98	0.84	0.53	0.70	0.43	0.04
3	40.55	14.45	17.11	47.71	24.12	6.41	54.12	49.01	33.43	7.52	36.36	22.79
4	45.26	53.59	36.57	52.54	59.94	40.33	51.21	30.95	27.35	28.85	22.77	32.54
5	43.20	56.58	44.28	65.83	52.85	54.89	39.39	16.82	ND*	11.38	22.35	18.17
6	16.75	36.69	21.76	19.54	38.97	42.15	22.26	28.82	3.51	1.50	0.42	29.72
7	30.89	16.27	13.09	12.03	17.29	20.52	55.04	10.36	2.33	6.97	16.91	8.16

ND* - Not Determined.

Annexure - 2.3.c. Distribution of clay (%) in the sediments of Cochin Estuarine System.

Stations	Nov-95	Dec-95	Jan-96	Feb-96	Mar-96	Apr-96	May-96	Jun-96	Jul-96	Aug-96	Oct-96	Nov-96
1	ND*	0.38	1.04	0.10	0.50	0.45	1.29	1.25	1.98	2.45	0.10	0.50
2	0.40	2.06	2.29	0.50	1.19	0.30	1.63	2.40	1.70	2.33	1.70	1.00
3	21.68	1.44	6.35	14.89	5.54	7.44	26.89	33.69	46.34	16.34	36.07	18.55
4	54.11	42.40	25.06	46.43	38.41	55.30	44.49	61.13	61.94	62.59	55.43	50.66
5	37.78	29.00	34.63	23.33	41.23	20.68	22.39	40.97	ND*	40.15	35.08	24.48
6	3.49	22.58	10.43	7.75	25.39	18.02	5.18	67.16	37.67	35.35	13.20	42.86
7	22.18	0.09	0.74	2.04	8.79	5.66	38.56	14.08	8.16	38.29	30.57	1.69

ND* - Not Determined.

Annexure - 2.4. Distribution of organic carbon in the sediments of Cochin Estuarine System (in mg/g)

Stations	Nov-95	Dec-95	Jan-96	Feb-96	Mar-96	Apr-96	May-96	Jun-96	Jul-96	Aug-96	Oct-96	Nov-96
1	ND*	1.03	1.61	0.53	3.12	1.41	1.41	0.82	0.27	0.68	0.36	0.48
2	3.63	2.76	2.44	2.58	0.76	3.25	3.25	2.65	0.27	0.72	0.36	0.86
3	15.3	7.01	8.54	8.22	4.86	5.75	5.75	0.82	13.49	4.78	8.59	7.48
4	19.65	17.02	11.25	11.11	11.47	10.41	10.41	6.11	0.46	10.62	8.02	8.78
5	12.3	14.72	8.79	6.98	15.02	10.62	10.62	8.58	ND*	5.33	6.56	5.41
6	6.61	19.13	9.06	4.66	8.04	1.18	1.18	6.87	4.38	4.75	5.92	12.22
7	12.53	5.72	5.95	4.8	8.73	7.79	7.79	0.69	8.33	6.51	3.5	5.77

ND* - Not Determined.

Annexure - 3.1 a. Distribution of Methylene Blue Active Substances in the surface and bottom waters of Cochin Estuarine System (in ug/l).

Stations	Nov-95	Dec-95	Jan-96	Feb-96	Mar-96	Apr-96	May-96	Jun-96	Jul-96	Aug-96	Oct-96	Nov-96
1. S	ND*	19.22	17.35	15.56	5.20	1.95	26.81	13.85	64.31	16.00	34.00	14.00
B	ND*	57.38	17.75	23.20	9.84	2.93	30.32	26.65	8.63	15.00	30.00	12.00
2. S	12.68	18.75	16.09	20.81	4.88	3.01	25.78	18.85	23.53	32.00	28.00	16.00
B	9.86	13.50	16.96	15.36	17.07	11.46	23.10	23.36	14.12	12.00	24.00	18.00
3. S	12.68	12.43	27.19	15.29	8.13	3.74	23.77	9.89	73.73	26.00	22.00	20.00
B	7.05	16.69	14.10	20.01	13.25	4.80	26.77	12.86	10.20	34.00	18.00	26.00
4. S	16.91	19.61	14.63	17.89	12.93	9.59	18.17	10.92	59.61	32.00	20.00	18.00
B	12.68	22.21	16.36	27.66	20.00	12.77	20.69	12.86	14.90	32.00	22.00	34.00
5. S	35.22	25.53	16.62	21.61	16.59	16.34	20.81	14.43	ND*	24.00	28.00	28.00
B	36.63	28.66	20.28	25.86	23.99	24.56	15.95	14.66	ND*	20.00	26.00	22.00
6. S	10.57	12.10	18.68	26.13	16.02	10.08	29.55	16.66	26.67	27.45	18.00	18.00
B	4.23	12.77	15.82	22.14	19.68	2.60	33.83	24.55	18.82	80.78	14.00	50.00
7. S	7.04	10.77	17.62	20.35	15.37	14.55	27.77	15.76	21.96	18.00	15.00	38.00
B	14.79	10.77	14.76	14.29	21.14	12.20	28.93	18.94	36.08	18.04	13.00	26.00

S - Surface; B - Bottom ; ND* - Not Determined.

Annexure - 3.1 b. Distribution of Methylene Blue Active Substances in the sediments of Cochin Estuarine System (in ug/g)

Stations	Nov-95	Dec-95	Jan-96	Feb-96	Mar-96	Apr-96	May-96	Jun-96	Jul-96	Aug-96	Oct-96	Nov-96
1	ND*	1.09	0.72	0.91	0.91	1.29	0.88	0.57	1.14	0.07	0.24	0.11
2	0.25	1.66	0.97	2.73	0.85	1.99	1.08	0.95	1.60	1.13	0.36	0.53
3	0.39	2.42	1.75	1.44	2.56	3.10	4.77	3.64	3.45	1.51	2.88	1.21
4	0.90	5.17	3.33	3.10	3.31	3.55	4.03	3.68	2.53	2.90	2.06	4.53
5	0.32	3.05	1.96	2.19	2.48	4.44	1.26	2.29	ND*	1.08	1.85	0.84
6	0.29	5.57	2.99	2.65	4.54	3.55	1.41	4.35	2.20	3.40	3.00	4.30
7	0.28	2.95	2.20	2.27	3.02	2.87	6.87	2.73	2.53	2.20	1.37	1.27

ND* - Not Determined.

Annexure - 3.2 a. Distribution of phenols in the surface and bottom waters of Cochin Estuarine System (in ug/l).

Stations	Nov-95	Dec-95	Jan-96	Feb-96	Mar-96	Apr-96	May-96	Jun-96	Jul-96	Aug-96	Oct-96	Nov-96
1. S	ND*	0.75	12.68	12.59	0.50	0.91	34.35	40.33	28.23	25.35	29.09	7.41
B	ND*	15.40	17.54	14.54	0.75	0.39	34.03	46.17	50.00	26.35	27.15	9.99
2. S	22.28	8.01	0.95	10.12	1.26	0.39	35.97	28.50	23.00	23.34	26.68	16.28
B	35.31	6.26	9.12	10.51	8.79	17.02	35.48	28.50	23.00	23.34	26.68	16.28
3. S	12.77	14.40	8.53	8.44	0.38	0.52	28.06	29.50	24.00	30.50	22.33	14.94
B	17.53	11.89	15.17	6.36	1.63	0.52	28.06	29.50	24.00	30.50	22.34	14.39
4. S	11.89	6.51	10.78	10.25	10.42	13.77	15.32	15.12	15.50	24.77	16.55	9.88
B	10.02	7.51	4.15	4.67	5.65	7.53	18.39	14.76	22.50	21.19	21.69	11.12
5. S	6.51	13.40	7.82	9.73	6.91	20.39	15.00	25.73	ND*	21.05	30.53	8.87
B	3.13	14.90	3.32	10.51	8.04	14.29	16.13	10.85	ND*	8.16	34.39	6.51
6. S	27.79	11.64	8.65	9.60	9.80	5.07	17.26	17.19	0.00	24.06	21.69	9.10
B	3.76	12.02	13.03	5.45	9.67	12.73	20.81	19.51	16.17	20.76	39.85	9.43
7. S	18.40	15.27	10.19	1.69	9.17	3.38	25.16	15.24	11.33	17.76	33.26	10.44
B	14.52	16.15	14.22	4.80	7.66	11.17	17.42	20.00	12.33	23.48	66.53	12.73

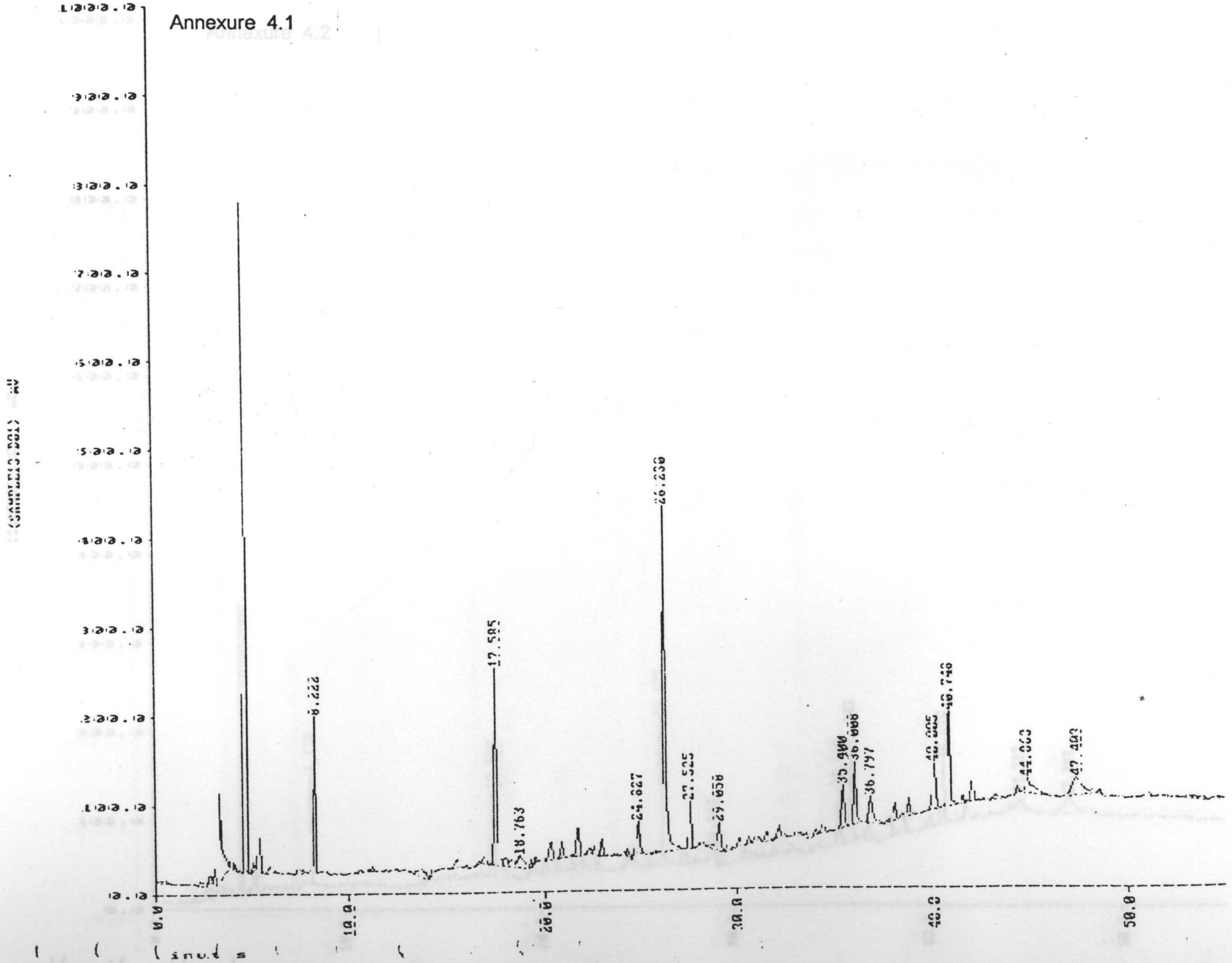
S - Surface; B - Bottom ; ND* - Not Determined.

Annexure - 3.2 b. Distibution of phenols in the sediments of Cochin Estuarine System (in ug/g)

Stations	Nov-95	Dec-95	Jan-96	Feb-96	Mar-96	Apr-96	May-96	Jun-96	Jul-96	Aug-96	Oct-96	Nov-96
1	ND*	0.67	5.28	0.39	3.97	1.04	1.70	0.00	0.03	0.27	0.38	46.17
2	1.55	0.54	0.00	3.56	14.41	3.80	0.42	0.00	1.17	0.00	8.27	0.57
3	7.56	0.02	0.00	0.94	0.94	1.10	8.89	1.63	0.82	4.34	0.38	21.06
4	9.41	2.32	0.00	5.55	28.27	1.08	9.87	61.57	7.27	13.53	0.00	4.53
5	0.22	0.58	8.10	5.15	5.09	5.37	0.00	13.36	ND*	2.42	35.18	36.77
6	1.69	1.45	19.92	1.72	4.28	1.10	0.00	0.00	0.60	0.00	1.12	3.36
7	0.94	2.31	7.78	1.98	1.61	14.54	7.16	9.65	0.31	4.64	35.04	12.13

ND* - Not Determined.

Annexure 4.1



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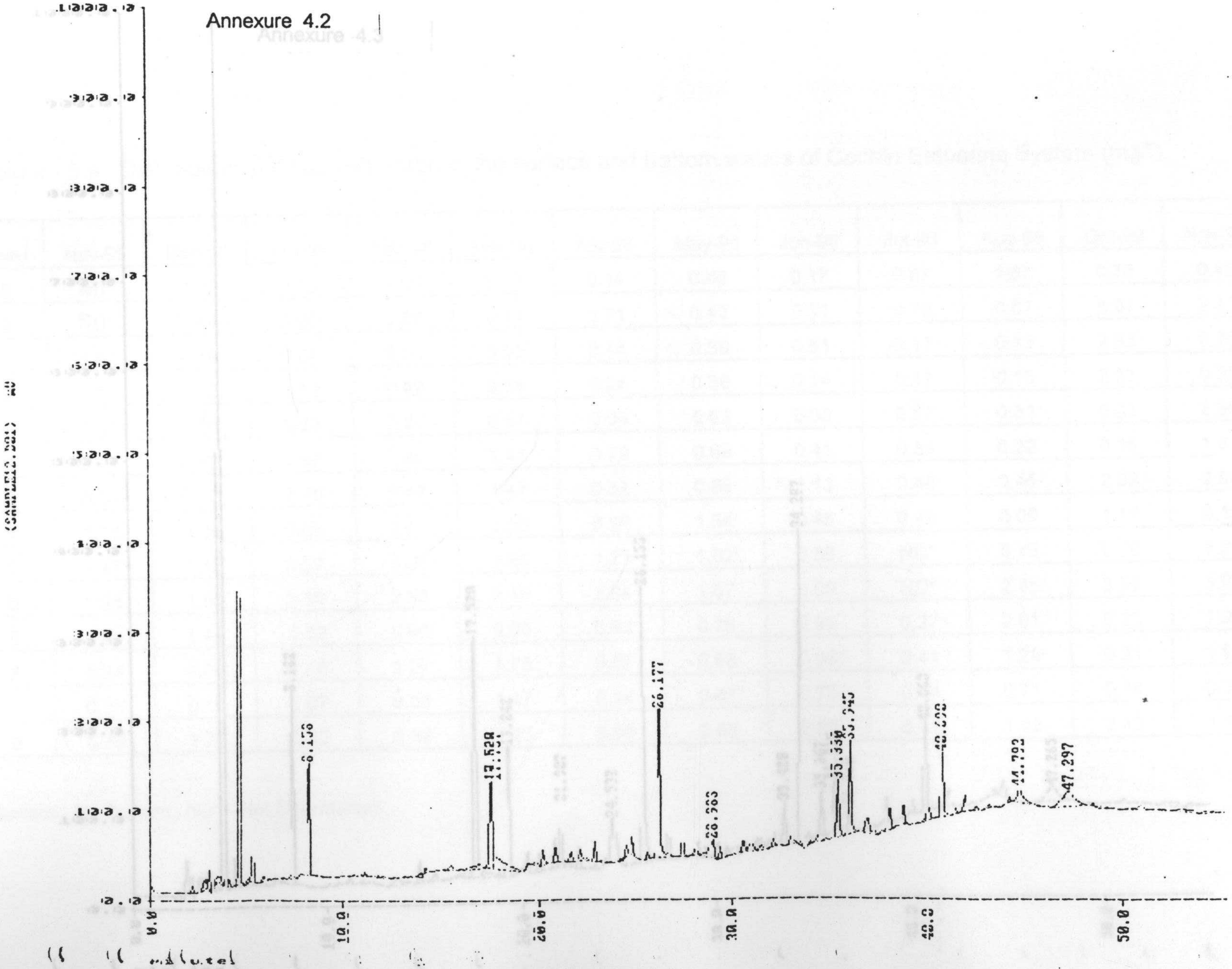
Annexure 4.2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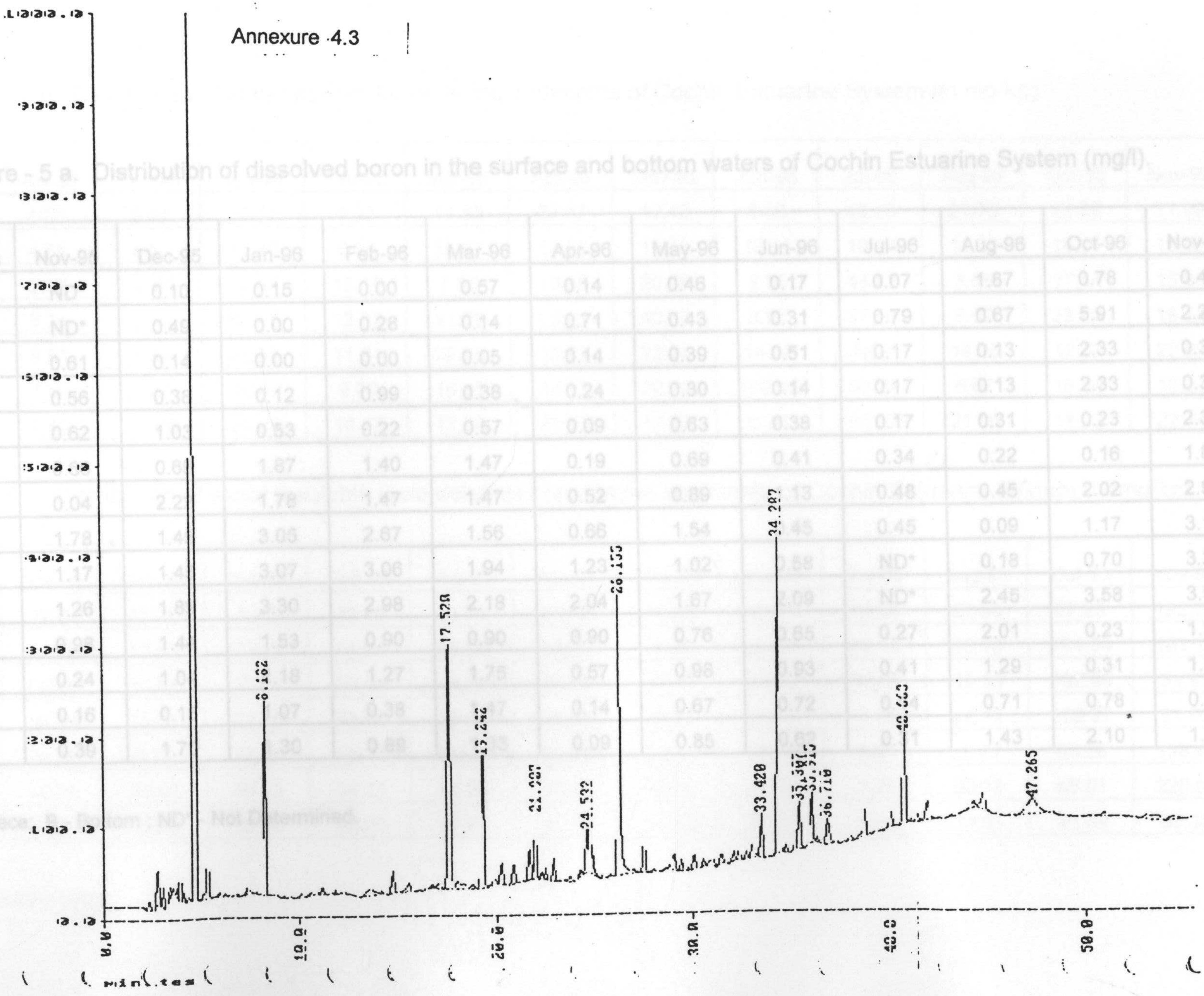
Annexure 4.3



Annexure - 5 a. Distribution of dissolved boron in the surface and bottom waters of Cochin Estuarine System (mg/l)

Stations	Nov-95	Dec-95	Jan-96	Feb-96	Mar-96	Apr-96	May-96	Jun-96	Jul-96	Aug-96	Oct-96	Nov-96
1. S	ND	0.10	0.15	0.00	0.57	0.14	0.46	0.17	0.07	1.67	0.78	0.49
B	ND*	0.49	0.00	0.28	0.14	0.71	0.43	0.31	0.79	0.67	5.91	2.23
2. S	0.61	0.14	0.00	0.00	0.05	0.14	0.39	0.51	0.17	0.13	2.33	0.36
B	0.56	0.38	0.12	0.99	0.38	0.24	0.30	0.14	0.17	0.13	2.33	0.36
3. S	0.62	1.03	0.53	0.22	0.57	0.09	0.63	0.38	0.17	0.31	0.23	2.36
B	[illegible]	[illegible]	1.67	1.40	1.47	0.19	0.69	0.41	0.34	0.22	0.16	1.87
S	0.04	[illegible]	1.78	1.47	1.47	0.52	0.89	[illegible]	0.48	0.45	2.02	2.90
B	1.78	[illegible]	3.05	2.67	1.56	0.66	1.54	[illegible]	0.45	0.09	1.17	3.12
5. S	1.17	[illegible]	3.07	3.06	1.94	1.23	1.02	0.58	ND*	0.18	0.70	3.21
B	1.26	[illegible]	3.30	2.98	2.18	2.04	1.67	[illegible]	ND*	2.45	3.58	3.97
6. S	[illegible]	[illegible]	1.53	0.90	0.90	0.90	0.76	0.65	0.27	2.01	0.23	1.96
B	0.24	[illegible]	[illegible]	1.27	1.75	0.57	0.98	0.93	0.41	1.29	0.31	1.92
7. S	0.16	[illegible]	1.07	0.38	1.47	0.14	0.67	0.72	[illegible]	0.71	0.78	0.27
B	0.39	[illegible]	1.30	0.89	[illegible]	0.09	0.85	0.62	[illegible]	1.43	2.10	1.12

S - Surface; B - Bottom ; ND* - Not Determined.

Annexure - 5 a. Distribution of dissolved boron in the surface and bottom waters of Cochin Estuarine System (mg/l).

Stations	Nov-95	Dec-95	Jan-96	Feb-96	Mar-96	Apr-96	May-96	Jun-96	Jul-96	Aug-96	Oct-96	Nov-96
1. S	ND*	0.10	0.15	0.00	0.57	0.14	0.46	0.17	0.07	1.87	0.78	0.49
B	ND*	0.49	0.00	0.28	0.14	0.71	0.43	0.31	0.79	0.67	5.91	2.23
2. S	0.61	0.14	0.00	0.00	0.05	0.14	0.39	0.51	0.17	0.13	2.33	0.36
B	0.56	0.38	0.12	0.99	0.38	0.24	0.30	0.14	0.17	0.13	2.33	0.36
3. S	0.62	1.03	0.53	0.22	0.57	0.09	0.63	0.38	0.17	0.31	0.23	2.36
B	0.66	0.69	1.87	1.40	1.47	0.19	0.69	0.41	0.34	0.22	0.16	1.87
4. S	0.04	2.22	1.78	1.47	1.47	0.52	0.89	1.13	0.48	0.45	2.02	2.90
B	1.78	1.45	3.05	2.67	1.56	0.66	1.54	0.45	0.45	0.09	1.17	3.12
5. S	1.17	1.45	3.07	3.06	1.94	1.23	1.02	0.58	ND*	0.18	0.70	3.21
B	1.26	1.89	3.30	2.98	2.18	2.04	1.67	2.09	ND*	2.45	3.58	3.97
6. S	0.98	1.44	1.53	0.90	0.90	0.90	0.76	0.65	0.27	2.01	0.23	1.96
B	0.24	1.04	2.18	1.27	1.75	0.57	0.98	0.93	0.41	1.29	0.31	1.92
7. S	0.16	0.18	1.07	0.38	1.47	0.14	0.67	0.72	0.14	0.71	0.78	0.27
B	0.39	1.70	1.30	0.89	1.33	0.09	0.85	0.62	0.31	1.43	2.10	1.12

S - Surface; B - Bottom ; ND* - Not Determined.

Annexure - 5 b. Distribution of water soluble boron in the sediments of Cochin Estuarine System (in mg/kg).

Stations	Nov-95	Dec-95	Jan-96	Feb-96	Mar-96	Apr-96	May-96	Jun-96	Jul-96	Aug-96	Oct-96	Nov-96
1	ND*	6.46	22.01	6.23	11.19	26.17	12.18	8.33	49.26	21.76	12.86	11.09
2	4.54	4.50	31.80	6.39	25.67	11.35	10.50	12.41	10.94	11.33	16.61	15.52
3	2.47	12.60	12.94	13.19	7.63	10.88	20.08	9.86	44.42	3.56	17.14	15.65
4	6.24	6.05	61.18	12.37	21.79	13.21	40.82	8.07	37.10	5.09	22.26	19.34
5	8.83	7.31	28.58	11.81	28.05	18.52	22.34	14.09	ND*	14.06	12.37	22.99
6	7.59	6.27	14.00	9.00	16.46	44.12	22.29	103.42	50.29	6.07	18.56	18.27
7	2.43	10.92	29.30	10.47	17.30	21.83	11.40	6.95	63.37	21.06	18.29	22.74

Anexure -5 c. Distribution of water insoluble (acid soluble) boron in the sediments of Cochin Estuarine System (in mg/kg).

Stations	Nov-95	Dec-95	Jan-96	Feb-96	Mar-96	Apr-96	May-96	Jun-96	Jul-96	Aug-96	Oct-96	Nov-96
1	ND*	11.26	5.42	13.60	31.72	54.49	24.94	16.31	50.59	27.90	67.25	182.60
2	51.06	13.53	134.08	14.64	49.85	58.46	20.66	20.35	72.53	46.18	191.54	181.16
3	118.98	10.88	20.14	20.44	48.89	15.24	37.54	43.82	80.58	12.68	137.99	31.77
4	110.68	13.52	42.33	53.64	38.07	26.76	23.20	21.87	5.16	14.12	132.27	51.05
5	70.50	9.77	73.68	158.52	122.94	30.68	23.47	20.23	ND*	67.07	83.28	136.43
6	12.31	20.95	38.03	14.16	14.37	37.47	24.26	65.25	7.26	60.12	45.01	220.50
7	7.74	9.60	30.29	15.65	49.86	99.95	21.43	55.32	6.61	11.67	35.84	69.30

ND* - Not Determined.