Chapter 3

Distribution of Surface Active Substances

3.1 Anionic Surfactant (MBAS)

Anionic surfactants are widely introduced in to the marine environment through out fall discharges or directly from wastewater treatment plants. The presence of surfactant organic matter in marine water is well known. Marine slicks formed both by natural and man made substances are clear proof of the existence of surfactant compounds. The significant changes in the dilatational properties of the sea surface, shown by means of the short gravity wave attenuation, constitute a specific characterisation and spreading and adsorption films (Lombardini et al., 1982; Scott, 1986; Cini et al., 1987). Surfactants are highly sorptive and become associated with sediments in the aquatic environments and sludges in wastewater treatment systems. Sludges often undergo anaerobic digestion and are disposed to soils.

Dissolved organic matter (DOM) is a large contributor to the pool of organic matter in fresh and marine water and thus plays an important role in the global carbon cycle (Cauwet, 1978; Mooper and Degem, 1979). In polluted waters the composition of organic matter is quite different Sontheimer (1976). Surface active substances form a major fraction of the DOC. Considering the industrial applications, human usage and aquatic discharges, the surface active substances present in the aqueous environment in this study can be grouped into two, the anionic surfactants and the phenolics.

3.1 Anionic Surfactant (MBAS)

Anionic surfactants are widely introduced in to the marine environment through out fall discharges or directly from wastewater treatment plants. The presence of surfactant organic matter in marine water is well known. Marine slicks formed both by natural and man made substances are clear proof of the existence of surfactant compounds. The significant changes in the dilatational properties of the sea surface, shown by means of the short gravity wave attenuation, constitute a specific characterisation and spreading and adsorption films (Lombardini et al., 1982; Scott, 1986; Cini et al., 1987). Surfactants are highly sorptive and become associated with sediments in the aquatic environments and sludges in wastewater treatment systems. Sludges often undergo anaerobic digestion and are disposed to soils.

Anionic surfactants in the aquatic environment are methylene blue active substances, which include linear alkylbenzene sulfonate (LAS), branched alkylbenzene sulfonate (ABS), alpha olefine sulfonate (AOS), fatty alcohol sulfate (AS) and fatty alcohol ethoxy sulfate (AES). There is little or no biological degradation of ABS in the aquifer, but LAS and NaLS detergents degrade fairly. Ammonium, ABS, LAS and Coprostanol are well-known pollutants originating from domestic wastes. Coastal and estuarine waters in some densely populated areas receive significant quantities of various derived chemicals, include anionic surfactants. Reports on these surfactants in marine and estuarine waters are relatively scare (Hon-Nami and Hanya, 1980; Ishiwatari, 1983) compared to the rather numerous studies on the occurrence and the behavior of LAS in the wastewater treatment and in natural waters (Painter and Zabel, 1988; Fell, 1989).

The presence of enhanced LAS concentrations could have a significant effect on marine fauna, especially in the first stages of development (Lewis, 1991). Moreover, it was shown that biodegradation of LAS in the marine part of the estuary was significantly slower than in its freshwater part (Terzic et al., 1992). Monitoring these pollutants using reliable analytical methods is, therefore, of great importance in preventing deleterious effects in estuarine and coastal environments.

Dispersion of LAS from sewage in to the lower part of the Karka River Estuary (Sibenic Harbor) was found to be highly significant in lowering the concentration, particularly under favorable wind conditions (Zutic and Legovic, 1987). High LAS concentration was found only in the immediate region of municipal waste water outlets (from 420 to 780 µg/l). After a distance of only 50 m from the sewage outlet the concentration dropped to only 7.2 µg/l and 3.2 µg/l, at depths 0.5m and 6 m, respectively. Further decrease in concentration was very slow, 1-2 µg/l, at the distance greater than 100 m. During longer periods of calm weather the wastewater plume can reach further parts of the Harbor. In such situations the concentration of LAS increased significantly in the freshwater layer but not in the saline water layer. The vertical distribution of LAS was characteristic for a highly stratified estuary. The concentrations were negatively correlated with salinity and the maximum was found at the microlayer (24 µg/l). The vertical transport of the pollutants was greatly reduced by the fresh and saline water boundary. Along with the biodegradation, dispersion and dilution also lead to decrease in the bioavailability of these compounds.

The Tamagawa, Sumidagawa, and Arakawa River comprise 24-40 % of the freshwater inflow to the Tokyo bay. In Tamagawa river, the LAS concentration varies from 0.78 to 4.49 mg/g; in Sumidagawa the values varies between 0.12 and 36.6 and in Arakawa the LAS con varies between 0.31 to 14.4 µg/g (Hideshige Takada *et al.*, 1992). A concentration range between 0.8 and 30 µg/l of LAS was found in Tokyo bay water and from below 0.2 to 69 µg/g (dry basis) for sediments.

The sum of concentration of 26 isomers of LAS, expressed as Σ LAS, in the sediments of Tokyo coastal zone range from 0.12 to 45.1 µg/g dry sediment (Hideshige Takada *et al.,* 1992). These are substantially lower than the concentrations found in the river sediments of Tokyo 36.3-567 µg/g (Takada and Ishiwatari, 1987), indicating that considerable amounts of LAS disappear during transport from the upper river to the estuary. The concentration of LAS decreases from >10 µg/g in the upper estuaries to <1 mg/g in the lower estuaries.

Temperature modifies the amount of biodegradation but not adsorption. Consequently, in winter biodegradation is minimum and LAS decrease was attributed to adsorption by the wet land. In the summer, decrease by biodegradation was larger than that of LAS in the inflow, and thus, LAS already adsorbed was also decreased (Kazuho Inaba, 1992).

The study on the variation of MBAS on the Sea water (Martinez *et al.,* 1989) collected from 2 miles offshore from Barcelona (J-1), the natural beach of Barcelona (CNB), a Mediterranean city with more than 2 million people and high urban and industrial activity; coastal water from Sant Feliu de Guixols (SFG) a small village with low pollution. Freshwater came from the Ebro River at its entrance to Amposta (Tarragona), a small village situated 30 km from the rivers mouth. Most of the surface samples analysed in this study contained <0.1 mg/l of MBAS. One of the cases occurred with seawater from CNB were 0.26 mg/l of MBAS was detected. The second case occurred when working with freshwater from the Ebro river, whose MBAS content was 0.34 mg/l. It is assumed that MBAS is a measure of anionic surfactants (natural or manmade), and other chemical products present in surface waters such as humic acids, proteins etc., as well as metabolites originated during the first step of biodegradation. However, intermediate biodegradation compounds of LAS are far less toxic than the same concentration of the intact compound (Brown *et al.,* 1978; Swisher *et al.,* 1964).

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The concentration of MBAS found in the samples collected from CNB varies between 0 to 0.26 mg/l with an average value of 0.066 mg/l. In SFG the value varies between 0 and 0.08 and in J-1, MBAS value varies between 0 and 0.11mg/l. The freshwater samples collected from the Ebro river has a concentration range of 0 to 0.34 and the average value for 9 samples will be 0.112 mg/l (Martinez, 1989).

The concentration of anionic surfactant in the Adriatic Sea at location > 1N mile offshore are low and rarely exceeds 10 µg/l. Higher values detected in the upper 5m layer in the north Adriatic during stratification periods are highly correlated with the influence of freshwaters of the river Po (Cosovic et al., 1979; Degobbis et al., 1979). Excessive surfactant contents and concentration of anionic detergents due to pollution by municipal and industrial sewage were detected in the Adriatic Sea only near by the pollution sources. Surfactant activity of seawater (MBAS) from West Istrian coast varies from ND to 0.620 mg/l (Kozarac et al., 1975).

The distribution of MBAS, alkyl benzene sulphonate in a small lake, Jyonuma Lake, in Tatebayashi, Gunma prefecture has a small surface area (about 0.5 km^2) and is relatively long and shallow average water depth about 1m. The river flows through Tatabayashi City, which has a human population of about 65,000. MBAS con in the water varies from 0.29 to 1.46 ppm, ABS con varies from ND to 0.6 ppm. In sediment MBAS varies from 107.3 to 377.8 µg/g (dry mud) and ABS varied from 16.9 to 96.3 µg/g (dry mud) (Uchiyama, 1979).

In Lake Suwa, one of the most polluted lakes in Japan situated in the central part, which has a diameter of 5 km and a maximum depth of 7 meters. The amount of ABS flowing in to the lake is estimated to be about 70 tons/year, and a considerable part of this deposited in the bottom of the lake. The content of MBAS in the lake mud was higher in the northern part of the lake, but in the south it was lower. Accordingly, ABS was higher in the north eastern part of the lake, especially in the region near Suwa city, where very high values (20-30 µg/g were found reflecting the pollution by the inflowing urban waste waters. Thus, the ABS absorbed on the suspended matters in the polluted river waters flowing in to the lake is considered to have deposited immediately after the mixing with the stagnant lake water (Yoshinari Ambe, 1973).

The MBAS concentration of Dong Hu lake water varied from 15 to 82 µg/l during September to November 1987 (Ayfar Yedilar *et al.,* 1989). The study on the effect of microbial population on the degradation of LAS shows there will be a good correlation between the LAS degradation rates and total bacterial population size was observed in all LAS experiments. Quality assurance procedures were undertaken to check the accuracy of the MBAS method in the study on a sample of distilled water spiked with 20, 40, 60, 80,100 and 120 µg/l. Seventeen analysts obtained means of 18.9, 39.2, 56.7, 74.2, 84.7, and 95.5 with an overall relative standard deviation of 0.009, 0.01, 0.03, 0.005 and 0.027.

In the surface water of Pacific Ocean surfactant (MBAS) concentration varied from 0 to 33 µg/l (Tkalin, 1987). The concentration of detergents in the upper meter of the northeastern part of Atlantic Ocean varied insignificantly, from 20 to 45 µg/l (Mikhaylov, 1978).

In Seawater, surfactant concentration increases due to rough sea condition and inland winds were likely to take place (were the synthetic surfactant concentration were low Oppo *et al.,* 1999). In Guido Bacci, Leghorn (Tyrrhenian sea, Italy), water samples collected during calm condition MBAS concentration varies from 0.005 to 0.009 mg/dm^3 and during rough time the concentration varies from 0.1 to 0.8 mg/dm^3.

3.1.1 Results and Discussion

The concentration of MBAS varies from 3.74 to 73.72 µg/l in the northern part of the Cochin estuary and 2.60 to 80.78 µg/l in the southern part (Annexure 3.1 a).

Seasonal values of MBAS showed high values in the surface water (fig: 3.1 a; Table 3.1, 3.2) during monsoon season compared to premonsoon and postmonsoon in the northern part. MBAS showed a decreasing trend from upstream to downstream during postmonsoon and in the southern part an increasing trend was observed in the bottom water during premonsoon and postmonsoon. No significant trend was observed in other seasons.

Station	1	2	3	4	5	6	7
Postmonsoon. S	21.14	18.30	18.86	17.83	26.67	16.47	17.69
B	29.28	16.46	16.37	21.45	26.71	19.36	19.?8
Premonsoon. S	12.38	13.62	12.73	14.65	18.84	20.45	19.?1
	16.57	16.?	16.21	20.28	22.59	19.56	19.?4
	.39	24.?		4.19	19.22		
					17.33		2?.?5

S - surface

Fig: 3.1 a

Table. 3.2 Seasonal average of MBAS in sediment (ppm).

Station	1	2	3	4	5	6	7
Postmonsoon	0.54	0.75	1.73	3.20	1.60	3.23	1.61
Premonsoon	1.00	1.66	2.97	3.50	2.59	3.04	3.?6
Monsoon	0.59	1.23	2.87	3.04	1.69	3.32	2.?9

In the premonsoon season, the MBAS showed maximum values in surface water during ... (38.?? µg/l in station. ?) and minimum value during Nov.'95 (?.?? µg/l in station ?). In the bottom water the anionic ... showed maximum ... July `96 (64.31 µg/l in station. 1) and the minimum value was during April `96 (1.95 µg/l in station 1) and June `96 (9.86 µg/l in station.3) respectively.

Fig: 3.1 b

In the bottom water, MBAS concentration showed maximum values during postmonsoon season during Dec`95 (57.38 µg/l in station.1) and minimum value in Nov`95 (?.? µg/l in station. ?)(fig. 3.1?). In the monsoon and premonsoon seasons the maximum value were observed ... (64.31 µg/l in station ?) ... May`96 (33.83 µg/l in station. ?) ... (8.63 µg ... station.1) and Apr. `96 (4.?? ...) ... showed very high values in the bottom water compared to other stations in the northern part during Dec. `95, Feb.96, May `96 and Jun.96, this may be due to the anthropogenic activities.
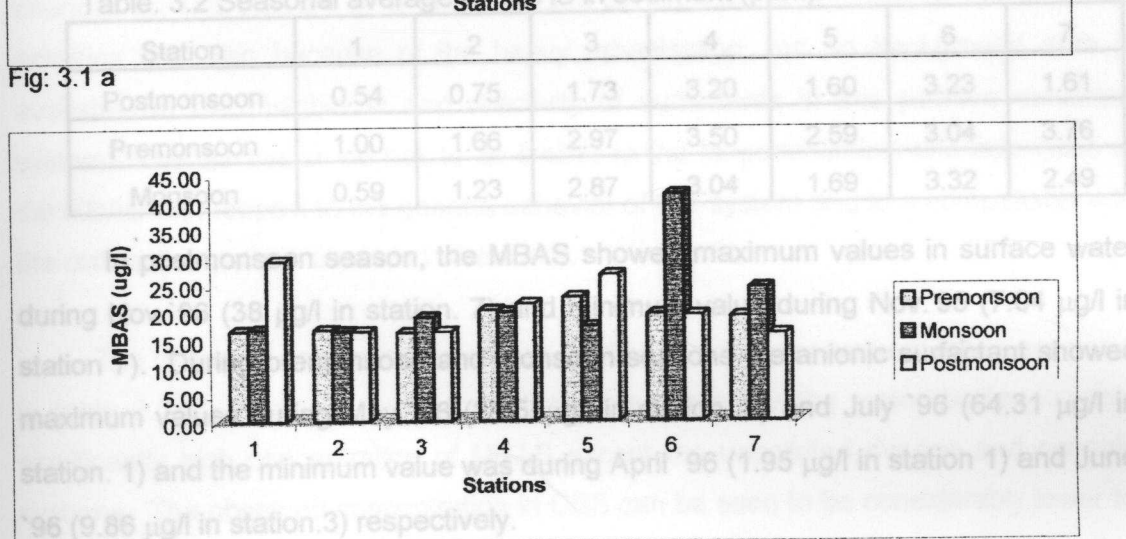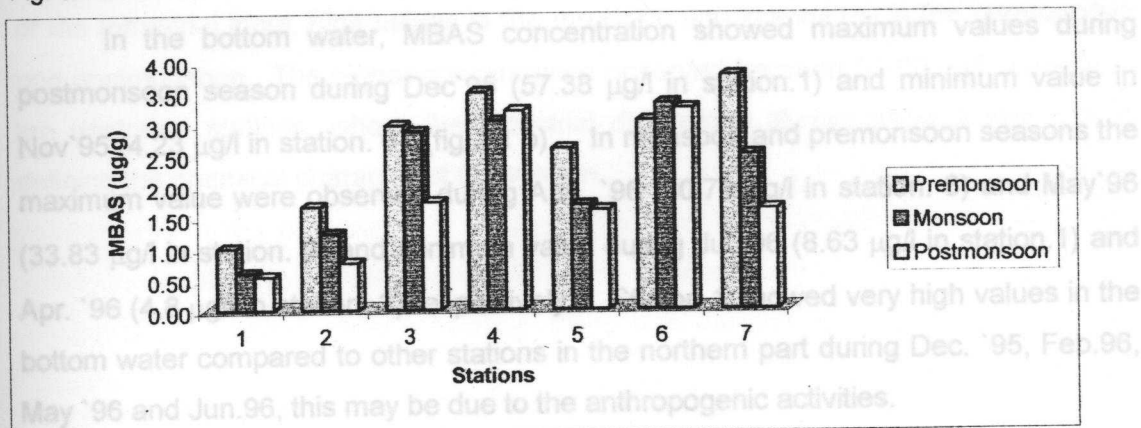

Fig; 3.1c

In the northern part of the estuary the MBAS concentration in the sediment varied from 0.075 µg/g to 4.77 µg/g and in the southern part the value varied from 0.28 µg/g to 6.87 µg/g (Annexure 3.1 b). No relationship between organic carbon, grain size and MBAS in the sediments of Cochin estuarine system was observed.

Table. 3.1 Seasonal average of MBAS in water (ppb).

Station	1	2	3	4	5	6	7
Postmonsoon. S	21.14	18.30	18.86	17.83	26.67	15.47	17.69
B	29.28	16.46	16.37	21.45	26.71	19.36	15.86
Premonsoon. S	12.38	13.62	12.73	14.65	18.84	20.45	19.51
B	16.57	16.75	16.21	20.28	22.59	19.56	19.14
Monsoon. S	31.39	24.79	36.54	34.18	19.22	23.59	18.57
B	16.76	16.49	19.02	19.92	17.33	41.38	24.35

S - surface; B - bottom

Table. 3.2 Seasonal average of MBAS in sediment (ppm).

Station	1	2	3	4	5	6	7
Postmonsoon	0.54	0.75	1.73	3.20	1.60	3.23	1.61
Premonsoon	1.00	1.66	2.97	3.50	2.59	3.04	3.76
Monsoon	0.59	1.23	2.87	3.04	1.69	3.32	2.49

In postmonsoon season, the MBAS showed maximum values in surface water during Nov.`96 (38 $\mu$g/l in station. 7) and minimum value during Nov.'95 (7.04 $\mu$g/l in station 7). During premonsoon and monsoon seasons the anionic surfactant showed maximum values during May `96 (29.55μg/l in station. 6) and July `96 (64.31 $\mu$g/l in station. 1) and the minimum value was during April `96 (1.95 μg/l in station 1) and June `96 (9.86 μg/l in station.3) respectively.

In the bottom water, MBAS concentration showed maximum values during postmonsoon season during Dec`95 (57.38 $\mu$g/l in station.1) and minimum value in Nov`95 (4.23 μg/l in station. 6) (fig 3.1 b). In monsoon and premonsoon seasons the maximum value were observed during Aug. `96 (80.78 $\mu$g/l in station. 6) and May`96 (33.83 μg/l in station. 6) and minimum value during Jul.`96 (8.63 $\mu$g/l in station.1) and Apr. `96 (4.8 μg/l in station. 3) respectively. Station 1 showed very high values in the bottom water compared to other stations in the northern part during Dec. `95, Feb.96, May `96 and Jun.96, this may be due to the anthropogenic activities.

In the northern part of the estuary the MBAS concentration in the sediment varied from 0.075 μg/g to 4.77 μg/g and in the southern part the value varied from 0.28 μg/g to 6.87 μg/g (Annexure 3.1 b). No relationship between organic carbon, grain size and MBAS in the sediments of Cochin estuarine system was observed.

MBAS in the sediment shows an increasing trend in all seasons from upstream to down stream in the north zone and showed high values in station. 4. (fig: 3.1c). In the south zone only during premonsoon there was a decreasing trend from upstream to downstream was observed, and in other seasons station.7 and Barmouth has low values compared to station.6.

Surface active substances in general and MBAS in particular are highly reactive in the aquatic systems. So building up of a high concentration in the natural water bodies is a rare chance. The earlier study on the distribution patterns of MBAS confirms this reactivity (Zutic and Legovic, 1987). In the CES there are abundant chances for the delivery of a huge amount of surfactants because of the industrial activities and also because of the heavy urbanisation, but no background data is available on the distribution and reactivity of surfactants in this positive estuarine system. The discussion so has to be limited to the biogeochemical characteristics of the MBAS with respect to the general behavior of this system and to a comparison with the distribution pattern observed elsewhere.

The observed concentration ranges of MBAS in different water masses are given in table 3.3. It can be seen from the table, generally the water bodies contain significantly high concentration of MBAS except the unpolluted riverine and oceanic systems. The observed concentration in CES can be seen to be considerably lower to the values observed elsewhere. The seasonal distribution pattern is a clear indication of the terrestrial input, high values in the monsoon and low values in the premonsoon and postmonsoon. The higher concentration observed between 50-80 µg/l, were from the upstream stations, where the industrial discharges always show a key role in defining the chemical character of the system.

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Table 3.3. MBAS concentration in water and sediment samples

Environment	Concentration	Reference
Lake Dong Hu.	15 to 82 µg/l.	Ayfer Yediler *et al.,* 1989.
Po. River	15 to 78 µg/l.	Galassi *et al.,* 1992
Seawater (Barcelona)	0.0 to 260 µg/l.	Martinez *et al.,* 1989.
Ebro river	0.0 to 340 µg/l.	Martinez *et al.,* 1989.
Pacific Ocean (surface water)	0.0 to 33 µg/l.	Tkalin, 1987.
Atlantic Ocean (northeastern part)	20 to 45 µg/l.	Mikhaylov, 1978
Jyonuma Lake (Tatebayashi)	290 to 1460 µg	Uchiyama, 1978.
Alexandra canal, Breakfast South, Cattai, French's, Middle Harbor, Oxford and Cowan creek.	190 to 900 µg/l	Pakalns *et al.,* 1978
Lane Cove river, Carrol, Ku-ring-gai and Neverfail creek.	30 to 80 µg/l	Pakalns *et al.,*1978
Jyonuma Lake sediment	107.3 to 377.8 µg/g	Uchiyama, 1978.
Cochin estuary	3.7403 to 73.7255 µg/l in the northern part of the Cochin estuary and 2.6019 to 80.7843 µg/l in the southern part (present study).	
Sediment	0.075 mg/g to 4.7734 mg/g in the northern part of the estuary and in the southern part the value varied from 0.2818 mg/g to 6.868 mg/g (present study).	

The observed distribution can, therefore, be compared only with unpolluted water bodies. The estuarine and down stream stations showed only very low values, though it will have contributions from the upstream and urban discharges. The major reason for this can be the high reactivity of MBAS, which is evident from the almost steady value at the Barmouth. It is also to be noted that MBAS does not give any correlation with any of the hydrographic parameters. It is clear, so, that the concentration of MBAS have a bearing, along with the mixing process, to pathways other than mixing.

From a station wise analysis of the data, one can see that more than the estuarine reactivity or characteristics it is the station characteristics that determines the concentration of MBAS. Though a decreasing trend towards the downstream is the overall character, the concentration values do have no interrelations or the trend is neither uniform nor have a direct relation to any of the general character of the estuary.

Sedimentary MBAS gave significantly high correlation with sedimentary organic carbon, thorough out the entire study. The seasonwise relationship and correlation coefficient values given in table. 3.4.

Table 3.4 Organic carbon vs MBAS in the sediment

Season		r	n
Postmonsoon	Y = 0.1447 x + 0.7437	0.51706#	34
Premonsoon	Y = 0.1032 x + 1.7841	0.39004*	28
Monsoon	Y = 0.148 x + 1.5528	0.49277*	20
Total	Y = 0.1151 x + 1.399	0.41987#	82

Y - organic carbon, x - MBAS in sediment
* - above 95% significance, # - above 99% sinificance.

The sediments of the CES, though the depth of water column is only about 3 m, were reported as having reducing environment (Vasudevan Nayar, 1992). Though one can infer from the increase of sedimentary MBAS concentration from the upstream to downstream that MBAS from the water column transported to the sediments during mixing process, the absence of the correlation between dissolved salinity and MBAS rules out this. No correlation between the sedimentary and dissolved MBAS was also observed. The correlation between the sedimentary organic carbon and sedimentary MBAS, indicate the operation of diagenitic processes that govern the diagenitic processes of organic matter, in the case of MBAS also. A differential but related diagenitic demineralisation was reported earlier also (Vasudevan Nayar, 1992; Beenamma Jacob, 1993). The pattern observed in the southern part of the estuary and the barmouth confirms this agreement. In these stations, the MBAS showed a decreasing trend towards down stream in premonsoon, which can be due to the increased diagenic activity. The shallow nature of the overlying water may be the reason. During monsoon and postmonsoon, these stations behaved similar to stations in the northern part.

In conclusion, the behavior of MBAS and the distribution pattern in water indicate that MBAS is not a potential pollutant in these waters at present. The sedimentary level, though, showed higher concentration, it is removed along with the general diagenic processes of organic matter.

3.2 Phenolic compounds (4-AAP method)

Application of appropriate separation techniques of DOC gave, for phenols of high river flow, the following main components: 36% small molecule biodegradable, 42% humic and fulvic acids, 10% sulphonated lignin's, 7% smaller sulphonated aromatics, and 5% chlorinated organic compounds. During periods of low flow the percentages shifted towards man-made pollutants, the latter three groups increased to 53% (Sontheimer, 1976).

In most natural waters, aquatic fulvic acids are a major fraction (20-80%) of DOC (Thurman, 1985). Aquatic fulvic acids comprise heterogeneous, yellow, biogenic organic acids; their formation is poorly understood. Fulvic acid molecules may be formed by condensation of smaller monomers released by degradation or they may be residual products of degradation of precursor macromolecules.

According to the polyphenol theory of humate formation, natural phenolic compounds are capable of being used as building units for the enzyme mediated synthesis of soil organic matter (SOM) or humus (Stevenson, 1982). Condensation of humate precursors may also results from abiotic reactions catalyzed by mineral oxides or clays (Shindo and Huang, 1984; Wang et al., 1978). Different processes involved in the synthesis of SOM can therefore result in the production of organic matter at different locations, which may be similar but not identical.

The highest permissible concentration of phenol in sea water should not exceed 1 µg/l (Buikema, et al., 1979) while polluted coastal waters, the concentration of phenol was found to be in the range of 2-15 µg/l (Baetman and Vyncke, 1979; Krajnovic, 1988).

In the past few decades anthropogenic activities have resulted in the introduction of several substituted phenols in to the soil environment. These compounds, which include chloro, bromo and alkyl phenols are different from naturally occurring phenolic materials. Some of these synthetic phenols can be incorporated in to humic macromolecules by various oxidative coupling reactions in a manner similar to natural humus formation processes (Bollag et al., 1980; Berry and Boyd, 1985 a).

The samples of final effluent collected from Sydney's three major sewage treatment plants contained the higher concentration of phenolics, which include the five chlorinated phenols. The chlorinated compounds are potentially more toxic and bioavailable than the phenols and cresols (Connell, 1988) and were readily bioaccumulated by mussels and the fish. The concentration of specific phenolic compounds were less than 150 µg/l, and after discharge through the deep water ocean outfalls those phenolics would be diluted to approximately 250:1 at the edge of the dilution zone, resulting in final concentration less than 0.6 mg/l. Again such concentration are unlikely to be acutely toxic, although chronic effects are possible.

The storm water samples contained low concentrations (0 to 1.7 µg/l) of eight of the ten phenolic compounds monitored including pentachlorophenol, with the most abundant compounds being o- and m-cresol and 2,4- dimethylphenol. These values, although low, may be of some concern in relation to both aquatic life and human health because these storm water drains discharge directly onto inter tidal and beach areas that are readily used as recreational areas and where little dilution occurs at low tide.

Concentration of phenolics in wet water storm-water flows were generally higher than after periods of dry weather, with most dry-weather samples containing only trace amounts of individual phenolic compounds (<.5 µg/l)(with the exception of Malabar and Greendale Creek, which had the highest concentration of pentachlorophenol). This is probable a result of flushing of roadways or possibly overflowing of the sewage system during rain, and the differences between the storm-water compositions of different drains could be accounted for by different land-use zones in each catchment.

In Ulhas estuary water samples with salinity range 5.3 to 35.8 ppt was analysed for phenols using 4-AAP. Concentration of phenolic compounds in this estuary varies from 0.00 to 23.5 µg/l (Kadam, 1996) and the highest value observed in the extreme upstream station. The value decreases with increase in salinity downstream. However, marginally high values were observed near the mouth of the estuary. The phenol concentration in surface waters during flood were 1.7 to 21.5 µg/l ranges, which decreases to 1.7 - 9.8 µg/l during ebb. Comparatively low values in bottom water and consistently high concentrations at upstream stations were the observations. The average concentration values increased from 0 to 16.4 µg/l towards upstream stations.

Krajnovic *et al.,* (1988) observed that the concentration of phenol during the experiments was decreasing and after a few days it dropped down to 50% of the initial values. This was attributed to the rapid proliferation of some phenolic bacteria, which have been demonstrated by inoculation of water samples from basins contain phenol, in to Bushnel- Hass culture media enriched with phenol only. From the basins containing 7.5 mg/l phenol the number of developing bacterial colonies was about 20 times higher than the control phenol free basins and they appear to be the main type of microorganisms population. It was suggested that moderate concentration of phenol in the marine environment do not represent a serious problem of pollution. It was also suggested that as in freshwaters (Trama, 1955; Kristoffersson, 1973) group of hetrotrophic bacteria prevent their excessive accumulation in the marine environment.

Sediments are major sinks for many phenols, and, in general, increasing substitution leads to an increase in their persistence in sediments. Phenol, because of its biodegradability is seldom detected in sediments. The same may be generally said about a number of other compounds such as the cresols, phenyl phenol, and the nonylphenol. By contrast some of these alkylphenols occur at remarkably higher concentrations, particularly near waste discharge site. Jungclaus, *et al.,* (1978) reported that two isomers of dibutylphenol reached 100-150 mg/kg in the sediments of Pawtuxet river, were as the corresponding maximum values for tributylphenol and dibutylmethyl phenol were 25 and 60 mg/kg, respectively.

Relatively little information is available on nitrophenols, methylphenols, and alkylphenols in water. One of reports (Jungclaus, 1978) indicated that the concentration of 11 alkyl phenols in the Pawtuxet river (USA) ranged from <1 to 6 μg/l. A similar range in values was reported for 4 -alkyl phenols in the Delaware River receiving both municipal and industrial wastes (Sheldon and Hites, 1978). Although nitrophenols were not found in either river, such compounds, especially trinitro-phenol, may be detected in rivers with input from munitions factory (USEPA, 1980).

Some phenolic compounds which occur in soil as degradation products of lignin's, humus and other polymeric materials are known to be toxic to plants Wang & Chung., 1967 McCalla & Hasking., 1964.). The phenolics formed as the intermediates in the microbial degradation are essential for the cycling of nutrients in the environment (Subba Rao, 1971; Knoesel, 1959). The detection of different phenolics in mangrove soils of Goa (Agacaim and Banastarim) could help in understanding the productivity of these regions (Karanth *et al.,* 1975).

Sediments contain a large amount of plant polymers like cellulose, amylose, pectin and lignin especially in mangrove. Lignin is resistant to bacterial attack, is decomposed mainly by white rot fungi to phenolic subunits (Burges, 1967). The latter are converted to polymeric forms and humus, which also serves as food material for fungi (Burges, 1967; Doetsch and Cook, 1973). Thus phenolic compounds also formed during the degradation of organic matter derived from plants (Stout et al., 1976). Molloy, 1976). Effluents are also one of the factors for increasing the phenol concentration in the ecosystem.

Par and Mindola estuary receive substantial quantities of phenolic compounds through the wastewater resulting in their occurrence in the receiving water in measurable quantities especially during low tides. The input of phenolics in to the estuary was 180 and 573 kg/day respectively. The low tide concentration of 32 µg/l at the mouth of par estuary increases to 1050 µg/l in the inner estuary. Although kolak estuary received only 22 kg/day of phenolics, the level in the receiving water are markedly high due to weak flushing (Zingde, et al., 1987).

In Kolak river the value of phenolics vary between 6-392 µg/l (Zingde, 1980). The phenolic content increased substantially at the down steam. The sharp increase in the phenolic content was considered to arise from GIDC industrial discharge that adds about 20 kg/day of phenolic compounds to the river water.

In Delaware Estuary, 4-AAP complexed phenolic compounds varied between 1-142 µg/l in water samples (Hunt et al., 1976) collected from 73 sites. In the upper estuary the phenolic concentration varies between 1-32 µg/l, in the lower estuary the values varies between 1-29 µg/l and in the shore samples the concentration is comparable with other stations which it varies between 1-142 µg/l. In mud samples collected from 58 sites, the phenolic concentration varies between 10 to 917 µg/g. Delaware Estuary receives many industrial and several petroleum refinery effluents, and is reflected in the phenol content.

The occurrence of total phenols was reported down stream from refinery outfalls in the region of Montreal (Polisois et al., 1975). Phenol concentration decreases with down stream distance from the source. Mass balance calculations at

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the many transverse sections indicated that this decrease in concentration was not attributed to dilution only. Microbially mediated degradation was a contributing factor.

Lignin, a phenolic polymer unique in vascular plants (Sarkanen & Ludwick., 1971), detected and quantified by the presence of individual phenols comprising the vanillyl, syringyl and cinnamyl families (Hedges & Man., 1979; 1962). Hedges & Ertel., 1982). Lignin contains about 15% free phenolic groups and is present in all of the dissolved humic and fulvic acids from the amazon river system (John R. Ertel *et al.,* 1986). Lignin phenols are released from these humic substances with the same efficiency as from vascular plants. Vanillyl phenols 30% and 90 % for syringyl phenols and estimated that up to 8% of carbon in humic acids and 3% of the carbon in fulvic acids are contained in chemically recognisable lignin structural units.

The photochemical reactivity of dissolved lignin and photobleaching of dissolved organic matter were examined in river and ocean water by Stephen Opsahl & Benner (1998). Approximately 75% of the total dissolved lignin in Mississippi River were lost during 28 d of incubation in sunlight, mostly due to photooxidation. The remaining fraction of dissolved lignin was much susceptible to photooxidation. About 90 % of the dissolved lignin in river water was present as high molecular weight (>1000 Dalton) DOM. However, after exposure to sunlight, about 80% of the remaining lignin was present as low molecular weight (<1000 Dalton) DOM. An absolute increase in concentration of LMW lignin provides direct evidence for the photo transformation of macromolecular DOM in to smaller molecules. The composition of riverine dissolved lignin also changed dramatically during photooxidation. The abundance of syringyl relative to vanillyl phenols decreased twofold, while concentration of vanillic acid relative to vanillin , increased four folds. The dissolved lignin in HMW DOM from the equatorial Pacific Ocean was highly resistant to photooxidation. This finding suggests that photochemical reactions play a prominent role in determining the composition and reactivity of terrigenous DOM in the Ocean (Stephen Opsahl & Benner (1998).

3.2.1 Results and Discussion

In the Cochin estuary, no high concentration of phenolic compounds was observed in the study. The seasonal values are given in the Table 3.5, 3.6. In the northern part the concentration varied from 0.389 to 50 µg/l where as in the southern

part values ranged from ND (not detected) to 66.53 µg/l (Annexure3.2a). Minimum seasonal variation is observed in the Barmouth region, the values been between 3.13 and 34.39. In the northern part, the highest value for phenolic compounds was shown by station 1 (50 µg/l) bottom water during July 1996. In the southern part bottom water of station 7 (66.53 µg/l) exhibited the maximum value during Oct.1996.

Table. 3.5 Seasonal average of phenol in water (ppb).

Station	1	2	3	4	5	6	7
Postmonsoon. S	12.48	14.84	14.59	11.12	13.43	15.77	17.51
B	17.52	18.73	16.26	10.90	12.45	15.62	24.83
Premonsoon. S	12.09	11.94	9.35	12.44	13.01	10.43	9.85
B	12.43	17.95	9.14	9.06	12.24	12.17	10.26
Monsoon. S	31.30	24.95	28.00	18.46	23.39	13.75	14.78
B	40.84	24.95	28.00	19.48	9.51	18.81	18.60

S - surface; B - bottom

Table. 3.6 Seasonal average of phenol in sediment (ppm).

Station	1	2	3	4	5	6	7
Postmonsoon	10.50	2.19	5.80	3.25	16.17	5.51	11.64
Premonsoon	1.78	5.53	2.97	11.19	3.90	1.78	6.32
Monsoon	0.10	0.39	2.26	27.46	7.89	0.20	4.87

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 the monsoon season, the average value of phenolic compounds in the surface waters of Cochin estuary along the Periyar River shows an increasing trend towards the upstream. In the southern part of the estuary also showed a similar trend as that of the north zone, where phenolic concentration shows high values in the upstream station (station 7). Highest value for phenolic compounds during the monsoon months in the northern part of the estuary was during June 96 (46.17 µg/l in station. 1) and in the southern part was in August 96 (24.06 µg/l).

The distribution of phenols during premonsoon indicates a similar trend to that of monsoon in the northern part of the estuary except in station 4 (fig. 3.2 a). But in southern part there is a decreasing trend towards upstream. The maximum concentration of phenolic compounds in the northern part during premonsoon months was observed on May 96 (35.97 µg/l in station.2) and minimum in April 96 (0.39 µg/l in

In post monsoon season, the average concentration of phenolic compounds in station 5 is close to that of premonsoon values and no specific trend was observed in northern part. In the southern part, there was an increasing trend towards upstream.
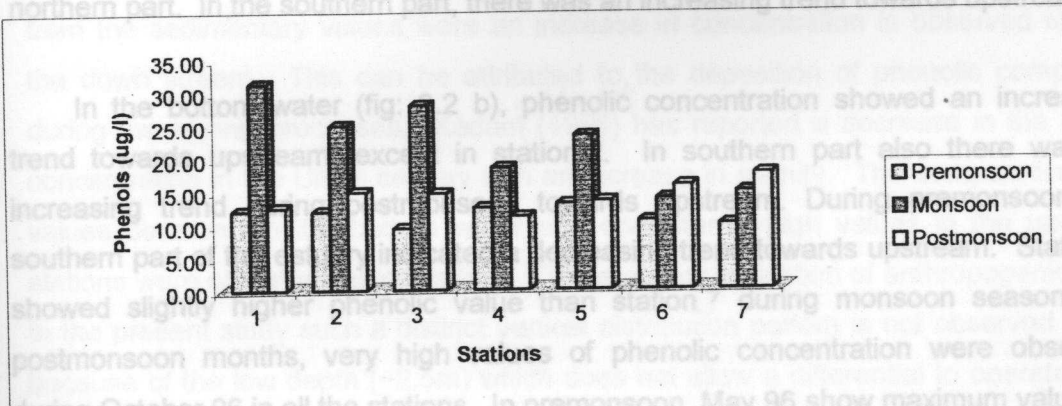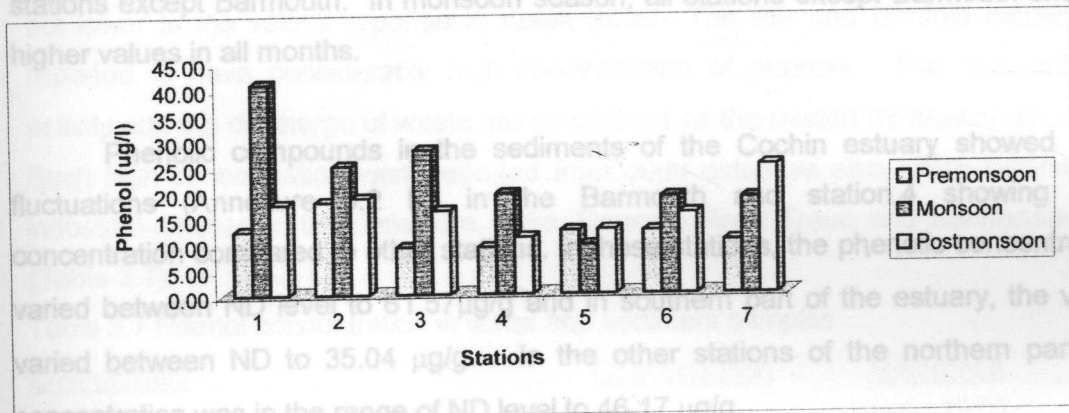
In the bottom water (fig. 3.2 b), phenolic concentration showed an increasing trend towards upstream except in station 5. In southern part also there was an increasing trend towards upstream of the estuary. During premonsoon, the southern part also showed an increasing trend towards upstream. Station.6 showed slightly higher phenolic value than station 7 during monsoon season. In postmonsoon months, very high values of phenolic concentration were observed during October 96 in all the stations. In premonsoon, May 96 show maximum values in stations except Barmouth. In monsoon season, all stations except Barmouth showed higher values in all months.

Phenolic compounds in the sediments of the Cochin estuary showed wide fluctuations. Annual average in the Barmouth area station recording high concentration. In the northern part of the estuary, the phenolic concentration varied between ND level to 6.57 µg/l and in southern part of the estuary, the value varied between ND to 35.04 µg/g. In the other stations of the northern part the concentration was in the range of ND level to 46.17 µg/g

Fig: 3.2 a

Fig: 3.2 b

Phenolic compounds in the sediment during monsoon showed an increasing trend from station. 1 to station 4 (fig 3.2 c) and in other seasons there is no specific trend and the southern area stations showed high value in all seasons compared to station.6. The concentration of phenols in the sediment was always very low in station 1, except in November 96 and of June 96.
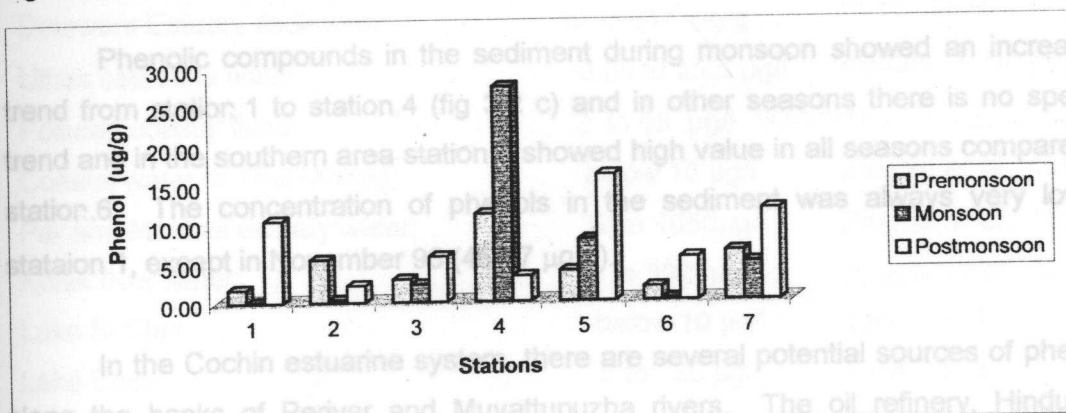
In the Cochin estuarine system, there are several potential sources of phenols along the banks of Periyar and Muvattupuzha rivers. The oil refinery, Hindustan Organic Chemicals and HIL discharge effluents containing phenols to the Muvattupuzha River. The sewage system is also used by many industries to dispose of there trade waste. Both the sides of the rivers are having high agricultural activities

Fig: 3.2 c

station.1). The maximum value in the south zone was during May '96 (25.16 µg/l in station. 7) and minimum value in February '96 (1.68 µg/l in station.7).

In post monsoon season, the average concentration of phenolic compounds in station 5 is close to that of premonsoon values and no specific trend was observed in northern part. In the southern part, there was an increasing trend towards upstream.

In the bottom water (fig: 3.2 b), phenolic concentration showed an increasing trend towards upstream, except in station.2. In southern part also there was an increasing trend during postmonsoon towards upstream. During premonsoon the southern part of the estuary indicated a decreasing trend towards upstream. Station.6 showed slightly higher phenolic value than station 7 during monsoon season. In postmonsoon months, very high values of phenolic concentration were observed during October 96 in all the stations. In premonsoon, May 96 show maximum values in stations except Barmouth. In monsoon season, all stations except Barmouth showed higher values in all months.

Phenolic compounds in the sediments of the Cochin estuary showed wide fluctuations (Annexure 3.2 b), in the Barmouth and station.4 showing high concentration compared to other stations. In these stations, the phenolic concentration varied between ND level to 61.57µg/g and in southern part of the estuary, the value varied between ND to 35.04 µg/g. In the other stations of the northern part the concentration was in the range of ND level to 46.17 µg/g.

Phenolic compounds in the sediment during monsoon showed an increasing trend from station 1 to station 4 (fig 3.2 c) and in other seasons there is no specific trend and in the southern area station 7 showed high 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 (46.17 µg/g).

In the Cochin estuarine system, there are several potential sources of phenols along the banks of Periyar and Muvattupuzha rivers. The oil refinery, Hindustan Organic Chemicals and HIL discharge effluents containing phenols to the Muvattupuzha River. The sewage system is also used by many industries to dispose of there trade waste. Both the sides of the rivers are having high agricultural activities

and there is a heavy input of vegetative matter and remains of agriculture to the river system.

The distribution pattern of the phenols in all the three seasons is indicative of considerable contribution from the land. The upstream stations can be seen to have considerably high concentration compared to the saline region, this is more evident from the sedimentary values were an increase in concentration is observed towards the down stream. This can be attributed to the deposition of phenolic compounds during the mixing processes. Kadam & Bhargale (1996) has reported a decrease in the phenol concentration in the Ulhas estuary with an increase in salinity. The comparatively low values observed in the bottom water and consistently high values in the upstream stations were observations of Kadam. This is a clear indication of anthropogenic input. In the present study such a distinct vertical distribution pattern is not observed mainly because of the low depth (~2.5m) which does not allow a differential to operate. The observed values are more or less high than that observed in the coastal waters of Thal, but lower than the values reported for Kolak River. The Par and Mindola estuary also reported to have considerably high concentration of phenols. The high industrial activity and the discharge of waste are considered as the reason for these high values. Such high concentration were reported from other estuaries also which receive high industrial discharge, the Delaware, Lake Traunse, River Traun and Sanfransiso Bay (Table 3.7).

Table 3.7 Phenol concentration in water and sediment samples

Environment	Concentration	Reference
Delaware Estuary and coastal water:	1-142 µg/l in.	Hunt., 1976
Delaware Estuary sediment:	10 to 917 µg/g	Hunt., 1976
Ulhas estuarine water:	0.00 to 23.5 µg/l	Kadam. & Bagle., 1996.
Polluted coastal water:	2 to 15 µg/l	Krajnovic-Ozretic, and Ozretic, 1988)
Coastal water of Thal (Alibag):	below 10 µg/l	Zingde et al., 1987.
Par and Mindola estuary water:	32 to 1050µg/l	Zingde et al., 1987.
Kolak river water:	6 to 392 µg/l	Zingde et al., 1980
Lake St Clair:	below 10 µg/l	EPA, 1973
Lake Erie:	5 to 30 µg/l	EPA, 1973
NorthWest Coast of India:	0 to 18.7 µg/l.	Kadam et al., 1992
Lower San Joaquin River and Suisun Bay:	2.2 to 30 µg/l,	James et al., 1962.
Lake Traunsee and River Traun:	8 to 45 µg/l.	Franz Bucher, 1993.
Mangrove sediments (Mandovi-Zuari)	0.26 to 1.01 mg/kg.	Helga R Gomas, 1982

The seasonal characteristics also indicate the dominance of terrestrial input to the phenolic content of the water as well as the sediments. Especially the monsoon values are clear indicative of such processes. The monsoon periods observed to have the lowest concentration in the bottom water, which is indicative of a low contribution from the seaside. The decreased flow in both rivers during the post and the premonsoon periods may be the reason for lowering the phenol content from that of the monsoon.

A few random exemptions, to the general trend, was one of the major observation, the localised effects may be the contributing factor. The average observed high value in station 4 Compared to station 5 can be due to the retting operations near the station 4 which releases a high load of phenolic compounds to the water. Another station to be specifically mentioned is station 2, which exhibited a higher concentration than station 1 during the premonsoon period. The low flow rate and the heavy industrial discharge may be the reason. A large number of industries including Fertiliser manufacturing drain just above station 2.

Except in the case of premonsoon, phenol gave significant correlation with salinity. The relation obtained is given in table 3.8. In sediment phenol gave correlation with organic carbon during premonsoon (table 3.9) and in other seasons there was no significant correlation.

Table.3.8 Correlation parameters: Salinity vs Phenol in water.

Season		r	n
Postmonsoon	Y = -0.3942 x + 18.429	0.35426#	68
Premonsoon	Y = -0.743 x + 12.661	0.08231	55
Monsoon	Y = -0.5362 x + 23.489	0.294412$	40
Total	Y = -0.392 x + 19.194	0.37464#	164

Y - Salinity, x - Dissolved Phenol in water

Table 3.9 Correlation parameters: Organic C vs Phenol in sediment

Season		r	n
Postmonsoon	Y = -0.5005 x + 11.915	0.21508	34
Premonsoon	Y = 0.4775 x + 1.8553	0.31277$	28
Monsoon	Y = 0.6823 x + 3.1082	0.19279	20
Total	Y = 0.0131 x + 6.3909	0.00558	82

Y - Salinity, x - Dissolved Phenol, *- above 95% significance,

- above 99% significance, $ - above 90% significance.

This indicates that mixing processes have significant effect on the distribution and reactivity of phenol. A significant correlation was observed between sedimentary phenol and sedimentary organic carbon during the premonsoon only. There can be two reasons for this, (1) the major pathways of degradation of phenols is not the general diagenic process. Phenols are considerably reactive in aquatic systems (Krajnovic-Ozretic, 1988) and so the sedimentary concentration of phenols are not reflections of the normal diagenic activity. (2) The reducing conditions prevailing in the sedimentary environment relatively restricts further diagenic processes. Considering the general reactivity of phenols, the first is the most probable in the CES.

In short, phenol has not become a potential pollutant in CES, even though there is significant contribution from land, mainly through industrial effluents. The positive character of the estuary and the reactivity of the phenols may be the contributing factors to this situation. A regular monitoring of the phenol content to keep the system in a sustainable condition is essential.

Chapter 4

Chlorophenolic compounds in the water and sediments

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 and form part of the food web. All these 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 (Olli-Pekka Penttinen, 1995). The wood pulp industries, which use different chlorine bleaching processes, are one of the main sources of organic chlorinated compounds. Chlorophenolic compounds have been reported to are the major constituents produced from lignin residues (Rogers & Keith., 1976). Some of them are toxic and can be accumulated in living organisms (Tian-Min Xie et al., 1986). Knowledge of chemical characteristics that affects environmental partitioning is required to evaluate environmental hazard (Widdows and Donkin, 1991; Depledge and Fossi, 1994).

4.1 Chlorophenols in the aquatic environment

Structurally, chlorophenols fit to the requirements of receptor-producing respiratory uncoupling. However, uncoupling oxidative phosphorylation is the mode of toxic action for chlorophenols with two or more chlorine substituents, while non-specific polar narcosis is the proposed mechanism in the case of mono substituted phenols

(Exon, 1984). However this division is not generally accepted. Schultz (1987) and Bryant and Schultz (1994) classified only the tetra chlorophenols and PCP as uncoupling agents, and the mode of toxic action of lower substituted chlorophenols were described as polar narcotics. In vitro studies have shown that even mono and dichlorophenols have instantaneous uncoupling properties (Ravanel et al., 1985, 1989; Tissut et al., 1987), although PCP is about 200 fold more potent uncoupler than mono substituted chlorophenols.

When PCP was added to an acclimated soil in concentrations of 10, 20, 40 and 80 mg/kg of soil by dry weight, a decrease in mineralisation was observed with increase in PCP concentration (Ramaprasad, 1994). The amount of PCP in solutions depends on several physical and chemical characteristics of soil such as pH, moister content, and bulk density (Justin Hurst et al., 1997).

The toxicity of chlorophenols can be considered as due to the three specific chemical characteristics (Terada, 1990); (1) an acid dissociable group (hydroxyl substituents), (2) a strong electron withdrawing moiety (halogen substituents), and (3) a bulky hydrophobic group (benzene ring). The hydroxyl group decreases hydrophobicity but increases reactivity (Bryant and Schultz, 1994). Replacement of the acid- dissociable group by a non-acid dissociable moiety results in complete loss of uncoupling activity (Terada, 1990). The addition of a chloro group increases both hydrophobicity, which dictates exposure, and the acidic strength (reactivity) of phenol. The more acidic the chlorophenol is, the more uncoupling the character of the chlorophenol (Saarikoski and Viluksela, 1982). Thus, the potency of chlorinated phenols in uncoupling oxidative phosphorylation depends on the degree of chlorine substitution (Shannon et al., 1991; Ravanel et al., 1989).

PCP is a general metabolic poison used extensively as a biocide in many industrial applications and as such is a contaminant in many water bodies (Rao, 1978; Jones, 1981). A primary action of PCP is the uncoupling of oxidative phosporylation (Weinbach, 1957; Weinbach and Garbus, 1965) along with other effects on energy metabolism (Bostrom and Johansson, 1972). The net effect is to increase the rate of energy metabolism in compensation for the reduced efficiency in ATP production. One important consequence of this is a reduced rate of growth, (Krenger et al., 1966; Webb and Brett, 1973; Hodson and Blunt, 1981; Holcobe et al., 1982; Sloof and Canton, 1983; Mathers et al., 1985).

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The majority of the organochlorinated compounds are high molecular weight chlorolignins (>1000). These are likely to be biologically inactive and have a small contribution to the toxicity, mutagenicity and BOD. They are stable against biodegradation, thus they cannot be removed by conventional primary and secondary treatment. However, long term, slow biodegradation of high molecular weight chlorolignins may cause environmental problems. Low molecular weight chlorinated neutral compounds are major contributors to mutagenicity and bioaccumulation due to their hydrophobicity and ability to penetrate cell membranes (Carlberg and Nashoaug, 1986; Heimburger et al., 1988a, b; Sun et al., 1989).

Wegman & Hofstee., (1979) studied the chlorophenols in the surface waters of the Netherlands during 1976-1977. In river Rhine the concentration of 2,4-, 2,5- and 2,6-dichlorophenol, 2,4,5- and 2,4,6- trichlorophenol, 2,3,4,6-tetrachlorophenol and pentachlorophenol had a frequency of occurrence of over 30%. However, in this period only the median values of the concentration of 2,6-dichlorophenol (0.15 and 0.1 μg/l), 2,4,6-trichlorophenol (0.19 and 0.18μg/l), 2,3,4,6-tetrachlorophenol (0.14 and 0.08 μg/l) and pentachlorophenol (0.73 and 1.1 μg/l) were found above the detection limit. In the Dutch part of the river Rhine the concentration of chlorophenols did not increase down stream. The concentration of PCP was maximum (11 μg/l) during the spring of 1977. In the river Meuse at Eijsden only the median values of the concentration of 2,3,4,6- tetrachlorophenol (0.06 and 0.05 μg/l) and PCP (0.38 and 0.79 μg/l) were above the detection limit. The concentration of chlorophenols found in a polderditch at Valkenberg was higher than those found in the river Meuse (Piet and De Grunt, 1975). The values reported were monochlorophenols 3-20 μg/l, dichlorophenols 0.03-1.5 μg/l and trichlorophenols 0.07 - 0.1μg/l.

In lake Ketelmeer, 2,5- dichlorophenol, 2,3,5 and 2,4,5- trichlorophenol, 2,3,4,5- and 2,3,4,6-tetrachlorophenol and PCP had frequency of occurrence of 100%

in sediment samples collected during 1979-1980 from 35 stations (Wegman *et al.*,
Van Den Broek 1983).   2- and 4-monochlorophenol and 2,3,6- trichlorophenol were never found
above the detection limit.   However, the detection limits for monochlorophenols were
much higher than those for other chlorophenols.   Median values of the concentration
in sediment samples of above 5 mg/kg were found for 2,5-, 3,4-, and 3,5-
dichlorophenol, 2,4,5-trichlorophenol and PCP.   The ratio of PCP in sediment to water
was 20.   Generally, the concentration in sediment was much higher than in water.
The sediment samples from the harbor and the Spui River was dumped in the North
Sea and were hardly contaminated with chlorophenols.   The contamination of the
Haringvliet River was comparable to that of Lake Ketelmeer.   The highest
concentrations of chlorophenols were found in the sediment samples from the Nieuwe
Maas River at Rotterdam and Vlaardingen, a highly industrialised area (Wegman *et al.*,
Van Den Broek 1983).

Bromophenols may be formed during chlorination of phenol in the presence
bromide ions.   The formation of 2,4,6-tribromophenol was reported under these
conditions (Janet A. Sweetman *et al.*, 1980).   A brominated phenol was observed also
& Simmons
in the process of chlorinating humic acid when chlorination was done from a system
containing bromide ion.

During 1979, a chemical spill occurred in Missouri as a result of train
derailment (U.S. Environmental Protection Agency, 1980).   The concentration of 2-
chlorophenol at the site reached a maximum of 1 mg/l on the day of the wreck,
decreasing to, 0.0015 mg/l within two months.   Bevenue *et al.*, (1972) reported PCP
residues of 0.002 to 0.27 µg/l in the snow of Maunakea Summit.   This resulted in the
PCP levels of 0.01µg/l in Lake Waiau, fed almost exclusively by the summit snows.
Arsenault (1976) found that PCP occurred at relatively high levels (max 0.3 mg/l) in the
air of wood-preservation plants.

Some of the highest values of PCP in water (306 - 895 µg/l) have been
reported for the Hayashida River (Japan), which receives uncontrolled input of leather
tannery wastes (Yasuhara *et al.*, 1981).   Elevated concentrations (10-100 µg/l) have
occurred in the Pawtuxet River (USA) owing to discharge from a chemical plant
(Jungclaus et al., 1978), whereas residues of 1-6 µg/l were reported for the Delaware
and Mississippi Rivers (Sheldon and Hites, 1978).

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15 of the 26 rivers sampled near the Great Lakes (Kuehl, 1981). Lower chlorinated anisoles and pentachloroanisole have also been found in fish from the Arkansas River and in fish exposed to municipal wastes (Veith et al., 1979).

Wolfgang Ernst & Weber., (1978) studied the distribution of PCP in the Weser river, estuary and German Bright (coastal area) from November 1976 to December 1977. They observed that PCP concentration in the water samples of Weser River and estuarine water varied from 49 to 496 ng/l. In the German Bight PCP level dropped near to the detection limit with increasing distance from the coastline, the value varied between <2 to 26ng/l. The highest value (26 ng/l) was due to the input from river Elbe and in the remaining stations the PCP concentration was below 10 ng/l. Tidal variations of the PCP- levels in Weser estuary clearly correlated to tidal fluxes resulting in highest levels at low tide, thus indicating the input of river-borne PCP.

In addition to PCP, six lower chlorinated phenols were identified and quantified. The sum of the chlorinated phenols in estuarine waters averaged 20% of PCP, 2,3,5,6- and 2,3,4,6- tetrachlorophenol and 2,4,6 trichlorophenol predominated. River input of chlorophenols can be derived from decreasing concentrations in the rivers way to the open sea. No change was showed in the comparing patterns of chlorophenol levels in water from different areas of the estuary (Weser, 1978).

Weber (1978) reported that PCP residues in the sediments of Weser estuary averaged 13 μg/kg dry weight compared with 0.3 to 1.5 μg/kg for dichloro-, trichloro-, and tetrachlorophenol. The coastal waters of British Columbia (Canada), where the effluents from a wood preservative plant was discharged had an average PCP concentration of 65 μg/kg, tetrachlorophenol 96 μg/kg and trichlorophenol 26 μg/kg (Jones, 1981).

In Tama River that covers 60% of the total Tokyo area a concentration of 1 - 9 x 10^2 ng/l were observed. In Sumida, which is, a tidal river in the central part of Tokyo had a concentration of 1-9 X 10^3 ng/l (Matsumoto et al., 1977)

In Danube River average chlorophenenols concentration ranged from 0.017 to 1.151 μg/l. The highest concentration measured for 2,4-dichlorophenol and the lowest for the isomers of tetrachlorophenol (Veningerova et al., 1998).

4.2 Results and Discussion

The chlorinated organic compounds in the aquatic environments are of great concern because of their persistence and toxicity. Chlorophenols, a class of compounds having considerably high industrial applications, form a significant fraction of the chlorinated organic compounds which pose considerable threat to restricted and semi enclosed water bodies. The detailed investigations on chlorophenols have identified about 19 of them, with varying number of chlorine and varying concentrations (Buikema *et al.,* 1979; Olli-Pekka Penttinen, 1995). A number of them are the result of industrial and urban discharges and the rest produced with in the system. In this study, due to unavailability of standards in the required purity, formal identification and assessment was done only for three of the species. Seven more prominent fractions were quantified with respect to o-chlorophenol and so the values reported here are only relative in the case of these seven fractions (Representative gas chromatograms are given in Annexure 4.1 to 4.3). In general fraction 6 are the most abundant in the CES and fraction 7 the least abundant. Trend given denote decrease or increase, as the case may, towards down stream (station 1 to station 4 in the north and station 7 to station 5 in the south).

In the Cochin estuary o-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 zone. In the southern part of the CES o-chlorophenol showed an increasing trend during postmonsoon in the bottom water and there was no significant trend for o-chlorophenol in the Cochin estuary (fig 4.1 a, b, c). Seasonal o-chlorophenol showed high values during monsoon season in the surface and bottom water, except in station 6 surface water during postmonsoon season. In the northern part of the estuary o-chlorophenol in the water samples varied from 2.03 to 43.32 ng/l and in the southern part the value varied from 3.5 to 376.75 ng/l (Table. 4.1 a). In the sediment samples o-chlorophenol showed a decreasing trend during monsoon season in the northern part of the study area and the station.5 showed the maximum value during monsoon (33.82 ng/l). In the northern part of the estuary o-chlorophenol varied from 8.93 to 28.36 ng/g and in the southern part the value varied between 7.1 to 33.82 ng/l (Table. 4.1b).
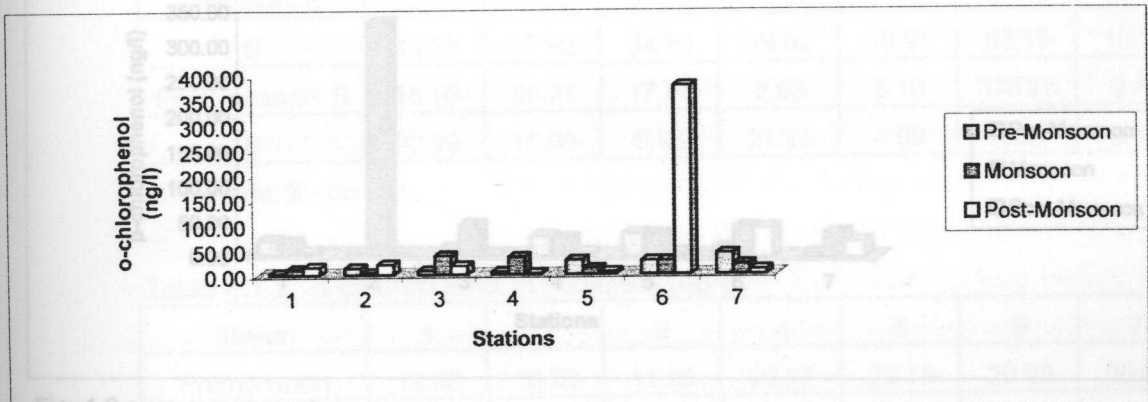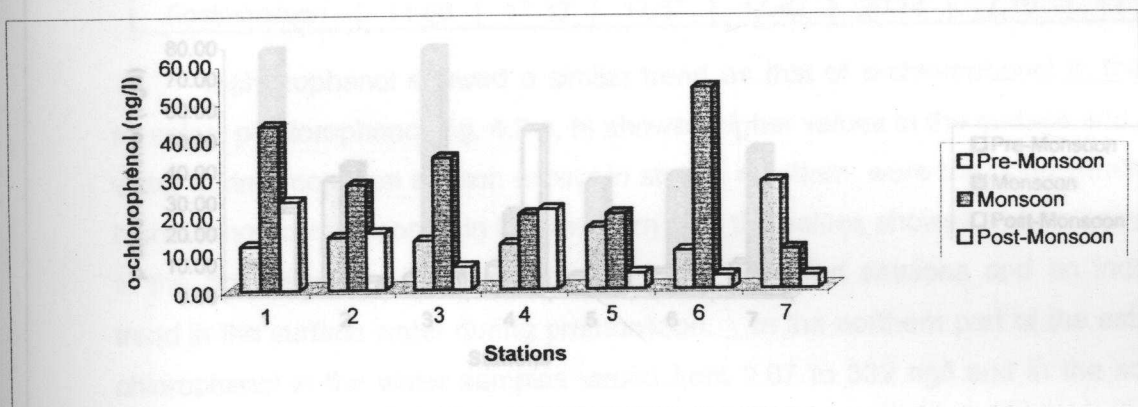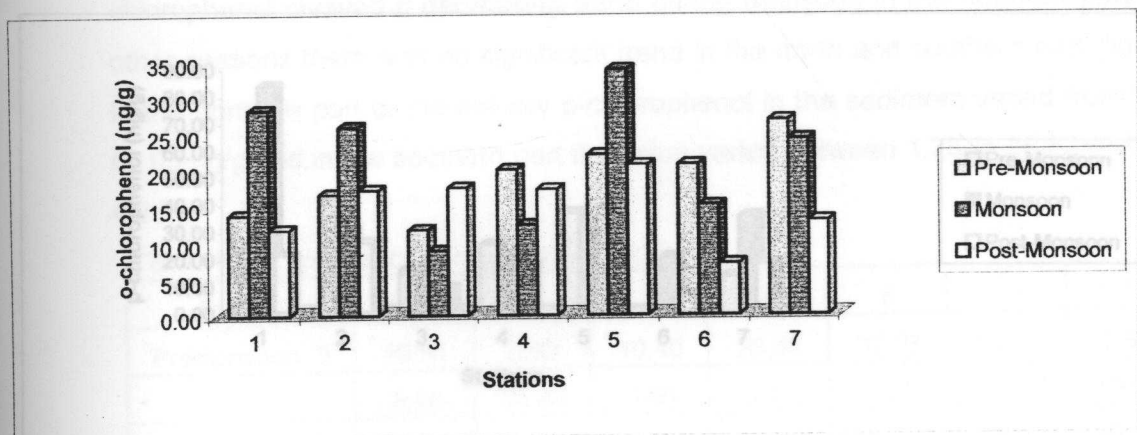
Fig: 4.1 a

Fig: 4.1 b

Fig: 4.1 c

Station	1	2	3	4	5	6	7
Premonsoon. S	2.91	13.13	8.14	5.47	28.74	27.11	41.76
B	11.74	13.84	12.96	12.00	16.23	9.94	28.28
Monsoon. S	10.73	3.39	37.62	34.50	11.89	27.39	20.44
B	13.32	27.83	34.90	19.92	19.91	53.15	10.37
Postmonsoon. S	15.16	20.31	17.18	2.03	5.10	376.75	9.41
B	23.39	15.06	5.95	21.15	4.09		
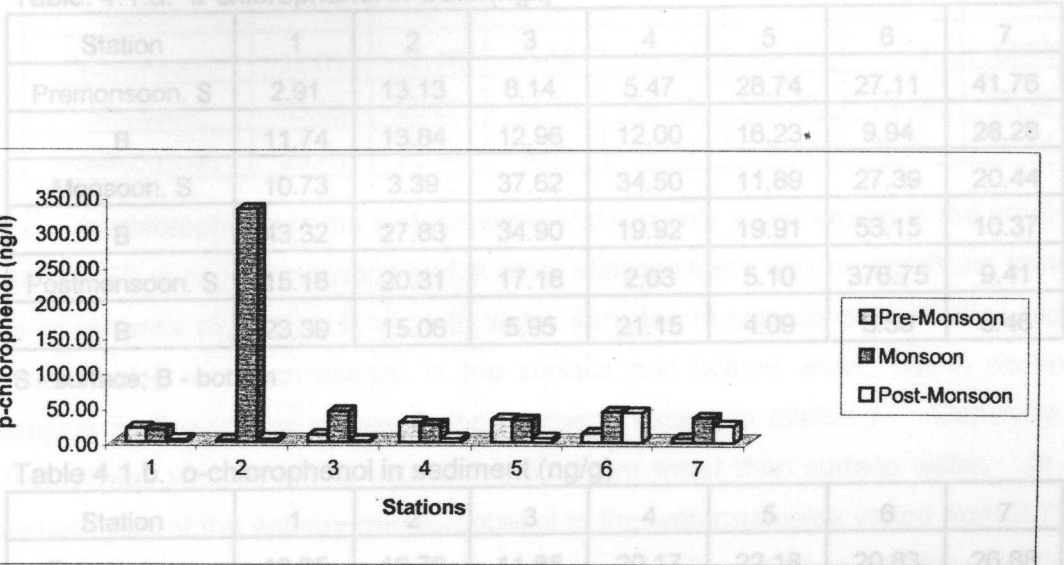
S - surface; B - bottom

Fig: 4.2 a

Table 4.1.b. o-chlorophenol in sediment (ng/g)

Station	1	2	3	4	5	6	7
Premonsoon	13.95	16.70	11.85	20.17	22.18	20.83	26.85
Monsoon	28.36	26.03	8.93	12.52	33.82	15.18	24.27
Postmonsoon	11.89	17.32	17.67	17.42	20.74	7.10	12.9

p-chlorophenol showed a similar trend as that of o-chlorophenol in the water samples. p-chlorophenol (Fig. 4.2 a, b) showed higher values in the surface and bottom water during monsoon season except in station 4 bottom, were the concentration was high during post monsoon. In the northern part, the values showed a ... trend in the monsoon and post monsoon seasons and an increasing trend in the surface water during premonsoon. In the northern part of the estuary p-chlorophenol in the water samples varied from 2.07 to 332 ng/l and in the southern part the value varied from 5.32 to 47.03 ng/l (Table 4.2 a). 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 (fig. 4.2 c). In the northern part of the estuary p-chlorophenol in the sediment varied from 9.05 to 85.0 ng/g and in the southern part the value varied between 1.33 to 20.52 ng/g (Table 4...

Fig: 4.2 b

Fig: 4.2 c

Table 4.2.a. p-chlorophenol in water (ng/l)

Station	1	2	3	4	5	6	7
Premonsoon. S	19.91		2.83	10.19	28.45	32.93	13.07	5.82
B	8.86	36.40	5.89	9.17	5.97	6.81	10.0
Monsoon. S	17.35	332.00	44.06	25.37	31.60	43.34	35.3
B	77.95	41.50	78.87	26.34	36.06	38.37	47.03
Postmonsoon. S	3.92	4.31	2.07	5.48	5.86	42.54	24.26
B	26.30	4.13	5.81	53.07	5.32	6.18	5.52

S - surface; B - bottom

Table. 4.1.a. o-chlorophenol in water(ng/l)

Station	1	2	3	4	5	6	7
Premonsoon. S	2.91	13.13	8.14	5.47	28.74	27.11	41.76
B	11.74	13.84	12.96	12.00	16.23.	9.94	28.28
Monsoon. S	10.73	3.39	37.62	34.50	11.89	27.39	20.44
B	43.32	27.83	34.90	19.92	19.91	53.15	10.37
Postmonsoon. S	15.16	20.31	17.18	2.03	5.10	376.75	9.41
B	23.39	15.06	5.95	21.15	4.09	3.50	3.46

S - surface; B - bottom

Table 4.1.b. o-chlorophenol in sediment (ng/g)

Station	1	2	3	4	5	6	7
Premonsoon	13.95	16.76	11.85	20.17	22.18	20.83	26.88
Monsoon	28.36	26.03	8.93	12.52	33.82	15.18	24.27
Postmonsoon	11.89	17.32	17.67	17.42	20.74	7.10	12.99

p-chlorophenol showed a similar trend as that of o-chlorophenol in the water samples, p-chlorophenol (fig. 4.2 a, b) showed higher values in the surface and bottom water during monsoon season except in station 4 bottom, were the concentration was high during postmonsoon. In the southern part, the values showed a decreasing trend in the bottom water during premonsoon and monsoon seasons and an increasing trend in the surface water during premonsoon. In the northern part of the estuary p-chlorophenol in the water samples varied from 2.07 to 332 ng/l and in the southern part the value varied from 5.32 to 47.03 ng/l (Table 4.2 a). 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 (fig.4.2 c). In the northern part of the estuary p-chlorophenol in the sediment varied from 9.05 to 83.05 ng/g and in the southern part the value varied between 1.73 to 38.52 ng/l (Table 4.2 b).

Table 4.2.a. p-chlorophenol in water (ng/l)

Station	1	2	3	4	5	6	7
Premonsoon. S	19.91	2.83	10.40	28.45	32.93	13.07	5.82
B	8.86	36.40	5.89	9.17	5.97	6.81	10.00
Monsoon. S	17.35	332.00	44.06	25.37	31.59	43.34	35.38
B	77.95	41.50	78.87	26.34	36.06	38.37	47.03
Postmonsoon. S	3.92	4.31	2.07	5.48	5.86	42.54	24.26
B	26.30	4.13	5.81	53.07	5.32	6.18	5.52

S - surface; B - bottom

Table 4.2.b. p-chlorophenol in sediment (ng/g)

Station	1	2	3	4	5	6	7
Premonsoon	22.81	42.10	15.60	24.97	36.71	1.73	13.68
Monsoon	83.05	30.27	14.13	20.61	34.00	20.54	36.06
Postmonsoon	20.75	25.44	9.05	17.22	38.52	6.52	18.56

m-chlorophenol in the surface water showed only a decreasing in the southern part of CES during premonsoon and in other seasons there was no significant trend in the study area (fig 4.3 a, b, c). 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. In the northern part of the estuary m-chlorophenol in the water samples varied from 2.71 to 163.36ng/l and in the southern part the value varied from 4.91 to 285.88 ng/l (Table 4.3 a). In the northern part of the estuary m-chlorophenol in the sediment varied from 6.53 to 87.99 ng/g and in the southern part the value varied between 18.42 to 84.32 ng/l (Table 4.3 b).

Table. 4.3.a. m-chlorophenol in water (ng/l)

Station		1	2	3	4	5	6	7
Premonsoon.	S	9.70	21.14	44.31	11.54	4.91	7.56	9.17
	B	32.66	2.71	4.38	39.25	11.90	20.81	14.61
Monsoon.	S	11.07	163.36	114.17	154.76	132.55	59.57	112.34
	B	111.87	70.96	140.29	117.13	285.88	40.63	125.94
Postmonsoon.	S	38.13	7.48	12.27	23.09	26.84	105.77	39.01
	B	5.41	16.08	106.40	6.14	7.78	48.82	5.53

S - surface; B - bottom

Table. 4.3.b. m-chlorophenol in sediment (ng/g)

Station	1	2	3	4	5	6	7
Premonsoon	12.69	42.48	6.53	46.50	55.53	84.32	48.97
Monsoon	87.99	38.62	15.12	32.74	45.16	51.68	39.05
Postmonsoon	8.81	12.58	48.51	39.42	18.42	60.17	30.37

The concentration values of o-, p- and m-chlorophenols in CES are more or less close to each other both in water and sediment. Though m-chlorophenol did not give any specific trend, the concentration of all monochlorophenols showed higher concentration in monsoon season. Considering this observation along with the general high reactivity of monochlorophenols, the observed concentration of monochlorophenols can be considered as of anthropogenic origin. Concentrations of

Fig: 4.3 a

Fig: 4.3 b

Fig: 4.3 c

monochlorophenols in most of the sediments are near to not detected level (Wegman ₹
Van Den Broeck et al., 1983). In this study, these compounds showed significant concentration in sediments. This may be due to the low depth and considerably high discharge through fresh water. The concentration in water confirms this possibility. The decreasing trends in the concentration of these compounds from upstream to downstream in the sediments also support this view.
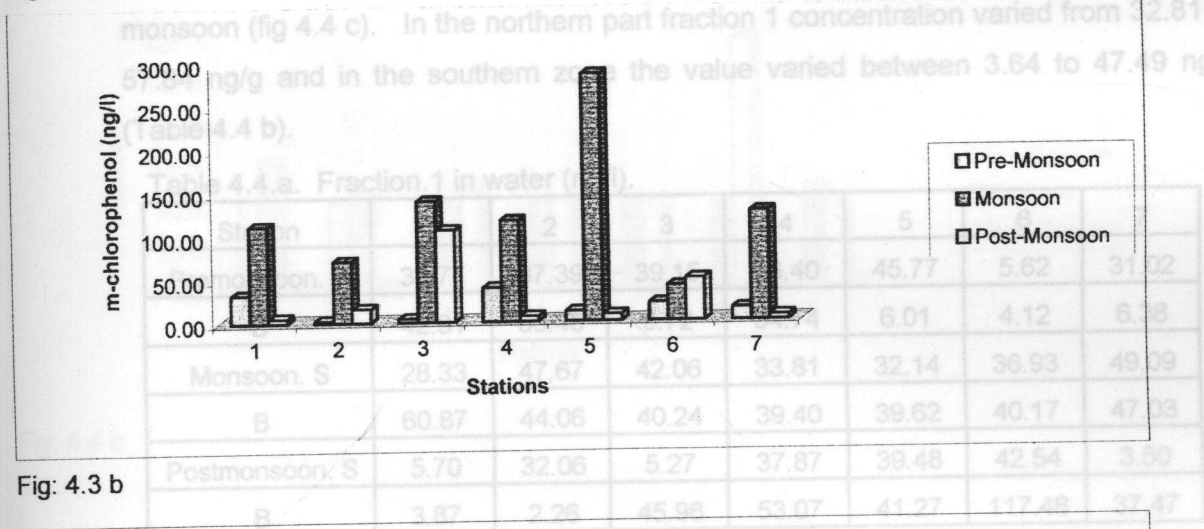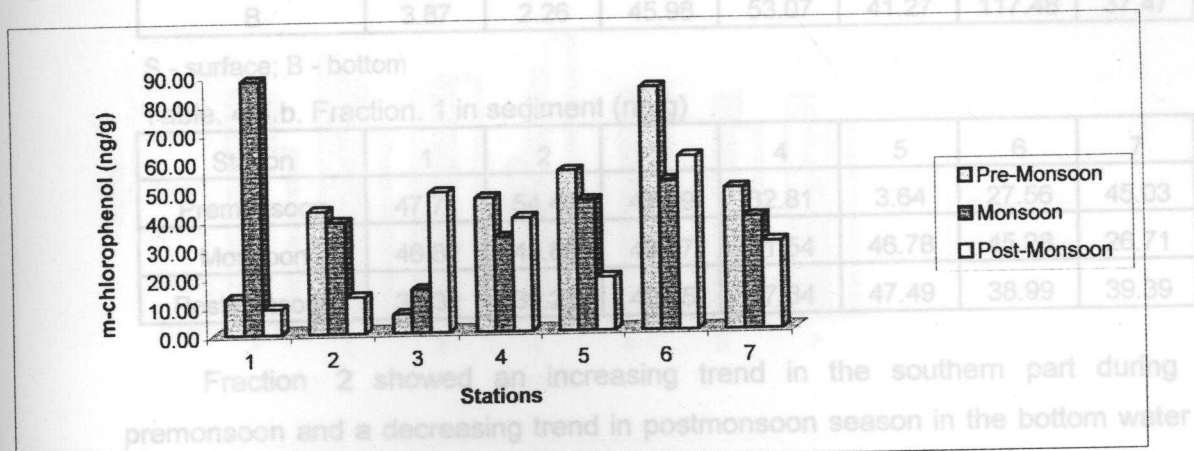
Fraction 1 showed a decreasing trend in the northern part of the estuary during monsoon in the bottom water. The surface water of the southern part also showed *a* the similar trend during monsoon and in other seasons the surface and bottom water gave no significant trend (fig 4.4 a, b). In the northern zone fraction 1 concentration varied between 2.26 to 60.87 ng/l and in the southern zone the value varied between 3.5 to 117.48 ng/l (Table 4.4 a). The sediment exhibited an increasing trend during monsoon and postmonsoon in the northern part and in the southern part during monsoon (fig 4.4 c). In the northern part fraction 1 concentration varied from 32.81 to 57.84 ng/g and in the southern zone the value varied between 3.64 to 47.49 ng/g (Table 4.4 b).

Table 4.4.a. Fraction.1 in water (ng/l).

Station	1	2	3	4	5	6	7
Premonsoon. S	39.77	37.39	39.15	36.40	45.77	5.62	31.02
B	42.31	39.48	9.72	34.74	6.01	4.12	6.38
Monsoon. S	28.33	47.67	42.06	33.81	32.14	36.93	49.09
B	60.87	44.06	40.24	39.40	39.62	40.17	47.03
Postmonsoon. S	5.70	32.06	5.27	37.87	39.48	42.54	3.50
B	3.87	2.26	45.98	53.07	41.27	117.48	37.47

S - surface; B - bottom

Table. 4.4.b. Fraction. 1 in sediment (ng/g)

Station	1	2	3	4	5	6	7
Premonsoon	47.71	54.48	47.69	32.81	3.64	27.56	45.03
Monsoon	46.82	48.85	49.97	51.54	46.78	45.28	26.71
Postmonsoon	35.32	39.25	49.55	57.84	47.49	38.99	39.39

Fraction 2 showed an increasing trend in the southern part during the premonsoon and a decreasing trend in postmonsoon season in the bottom water (fig 4.5 a, b). The sediment and surface water had no significant trend in the study area (fig 4.5 c). The fraction 2 varied between 16.19 to 95.76 and 23.73 to 74.79 ng/l for the northern and southern zones respectively (Table 4.5 a). In sediment samples

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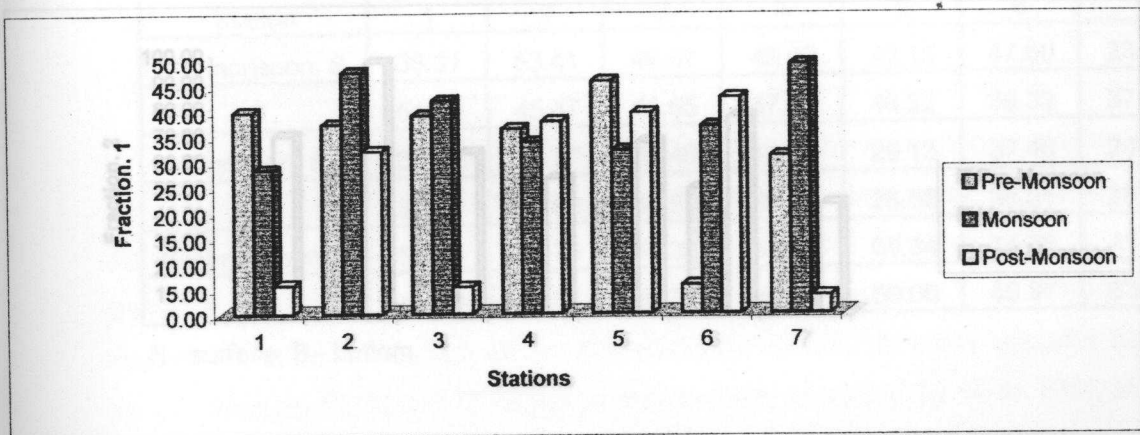
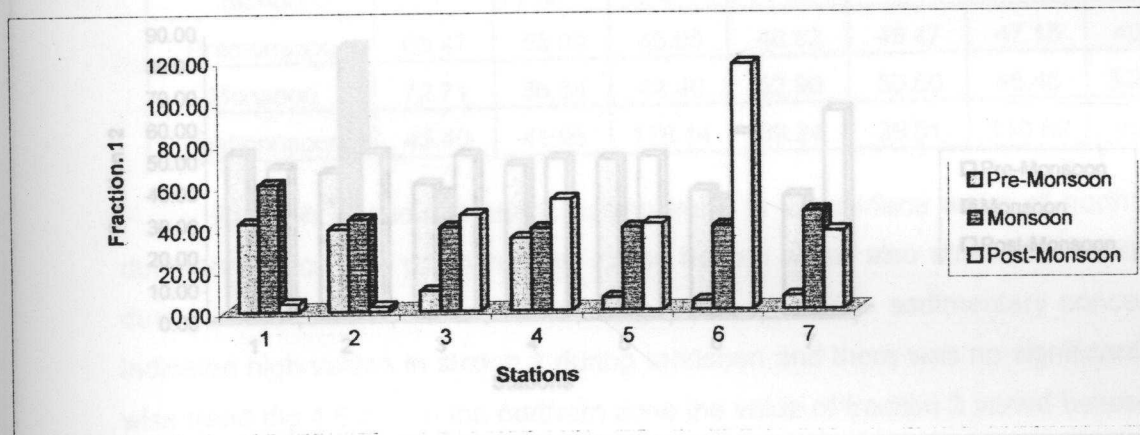Fig: 4.4 a

Fig: 4.4 b

Fig: 4.4 c
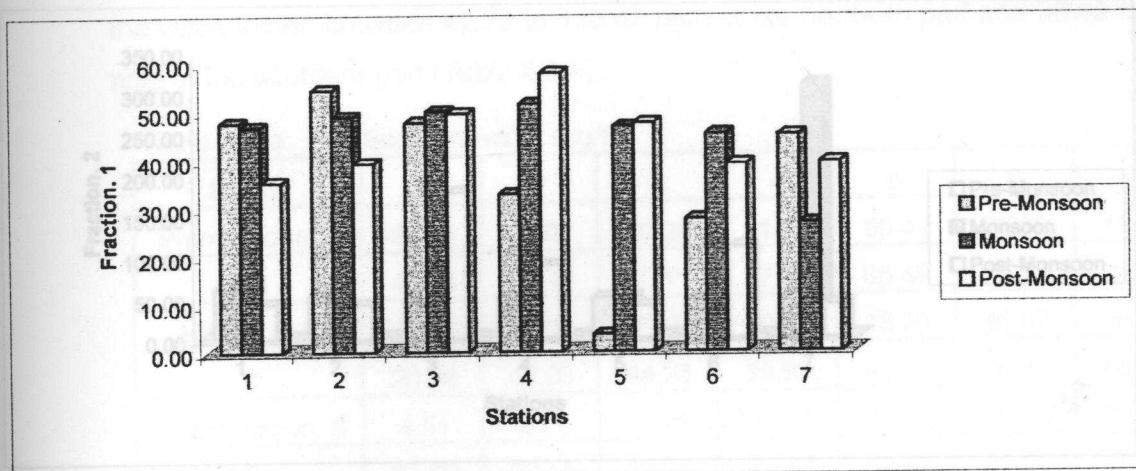
Fig: 4.5 a

Fig: 4.5 b

Fig: 4.5 c

fraction 2 varied between 36.64 to 178.14 ng/g in the northern part of the estuary and 39.51 to 308.95 ng/g in the southern part (Table 4.5 b).
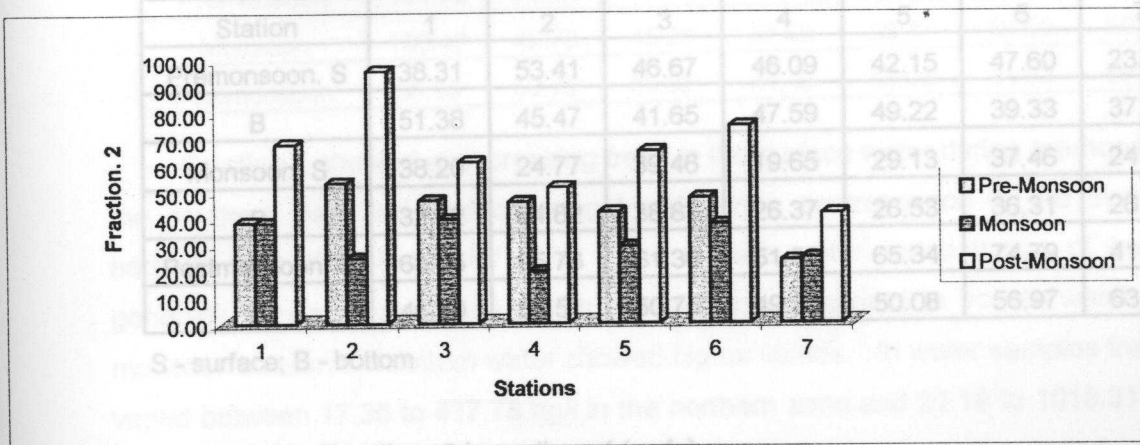
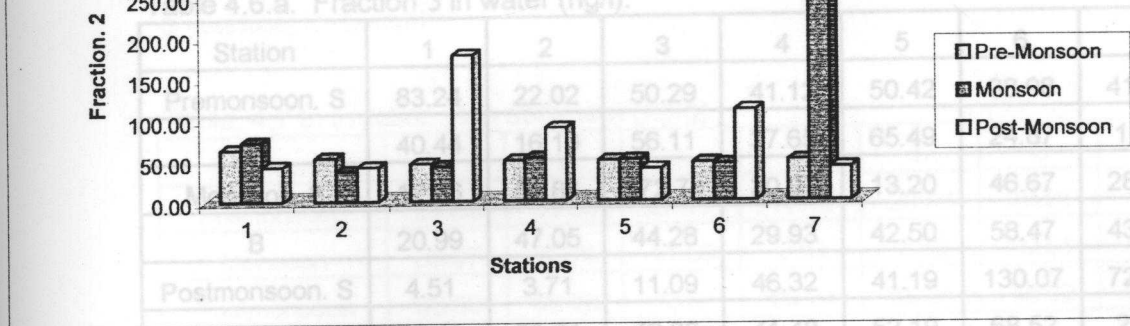Table 4.5.a. Fraction 2 in water (ng/l).

Station	1	2	3	4	5	6	7
Premonsoon. S	38.31	53.41	46.67	46.09	42.15	47.60	23.73
B	51.38	45.47	41.65	47.59	49.22	39.33	37.51
Monsoon. S	38.20	24.77	39.46	19.65	29.13	37.46	24.74
B	32.72	84.82	38.83	26.37	26.53	36.31	26.41
Postmonsoon. S	68.05	95.76	61.30	51.55	65.34	74.79	41.59
B	46.80	51.51	50.75	49.39	50.08	56.97	63.98

S - surface; B - bottom

Table. 4.5.b. Fraction 2 in sediment (ng/g).

Station	1	2	3	4	5	6	7
Premonsoon	63.47	53.04	45.85	49.52	49.47	47.15	49.73
Monsoon	72.71	36.64	42.40	52.90	50.60	45.46	308.95
Postmonsoon	42.40	41.95	178.14	89.24	39.51	110.89	40.91

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 (fig 4.6 a, b). The sedimentary concentration indicated high values in station 1 during monsoon and there was no significant station wise trend (fig 4.6 c). In the northern zone the value of fraction 3 varied between 3.71 to 172.74 ng/l and 1.27 to 130.07 ng/l in the southern part (Table 4.6 a). In sediment the value varied between 42.73 to 133.47 ng/g in the northern part and 36.69 to 73.35 ng/g in the southern part (Table 4.6 b).

Table 4.6.a. Fraction 3 in water (ng/l).

Station	1	2	3	4	5	6	7
Premonsoon. S	83.24	22.02	50.29	41.12	50.42	38.98	41.91
B	40.44	16.19	56.11	37.65	65.49	24.87	1.27
Monsoon. S	17.66	51.84	172.74	30.97	13.20	46.67	28.97
B	20.99	47.05	44.28	29.93	42.50	58.47	43.54
Postmonsoon. S	4.51	3.71	11.09	46.32	41.19	130.07	72.29
B	27.89	22.51	48.28	41.48	52.19	68.52	2.35

S - surface; B - bottom

Table. 4.6.b. Fraction 3 in sediment (ng/g)

Station	1	2	3	4	5	6	7
Premonsoon	101.72	71.42	76.98	83.07	68.80	73.35	66.25
Monsoon	133.47	42.73	45.26	52.69	68.47*	36.69	50.86
Postmonsoon	56.85	50.78	69.62	44.46	68.09	44.83	58.29

Fraction 4 showed an increasing trend in the surface water during premonsoon in the southern part and a decreasing trend during postmonsoon in the surface of northern part of CES (fig 4.7 a, b). The surface water concentration of fraction 4 generally showed high values during premonsoon compared to bottom water and in monsoon season the bottom water showed higher values. In water samples fraction 4 varied between 17.36 to 417.78 ng/l in the northern zone and 21.19 to 1018.31 ng/l in the southern part (Table 4.7 a). In the sediment samples the value varied between 2.93 to 69.08 ng/g in the northern part and 7.49 to 59.91 ng/g in the southern part of the estuary (Table 4.7 b). The sedimentary concentration also showed a decreasing trend during premonsoon and monsoon of the southern part and monsoon in the northern part of the estuary (fig 4.7 c). But in postmonsoon season, the southern part of the estuary showed an increasing trend.

Table 4.7.a. Fraction 4 in water (ng/l).

Station	1	2	3	4	5	6	7
Premonsoon. S	225.70	166.38	185.76	277.83	280.13	113.24	59.04
B	41.50	178.74	134.40	194.13	162.83	86.28	101.49
Monsoon. S	82.07	166.56	78.74	38.71	21.19	51.97	57.41
B	165.37	153.99	175.20	17.36	30.82	148.16	77.11
Postmonsoon. S	132.44	130.16	77.48	92.61	87.44	1018.31	317.17
B	182.05	101.31	408.42	417.78	72.38	172.99	113.01

S - surface; B - bottom

Table. 4.7.b. Fraction 4 in sediment (ng/g)

Station	1	2	3	4	5	6	7
Premonsoon	21.83	51.08	27.77	11.16	20.04	28.91	49.53
Monsoon	39.97	12.76	11.60	2.93	7.49	20.51	45.54
Postmonsoon	80.69	69.08	40.64	68.24	59.91	48.02	36.89

Fraction 5 generally showed high values in the surface and bottom water during premonsoon season in the northern part of the estuary except in station 1 surface, where high values were observed during monsoon. In the surface water
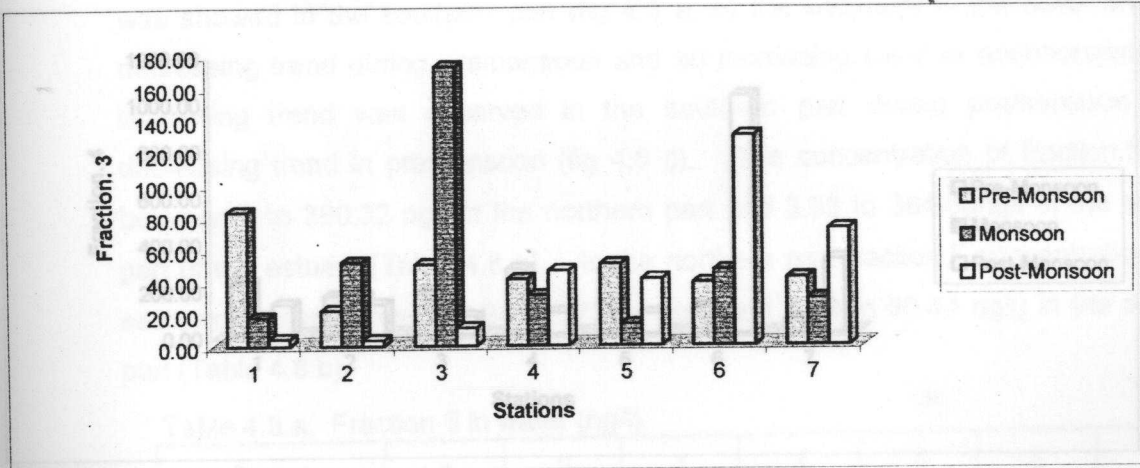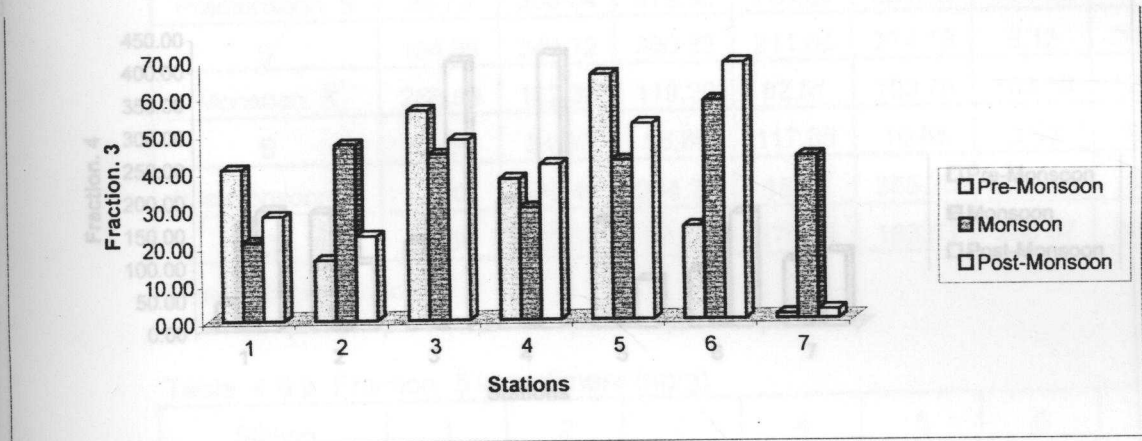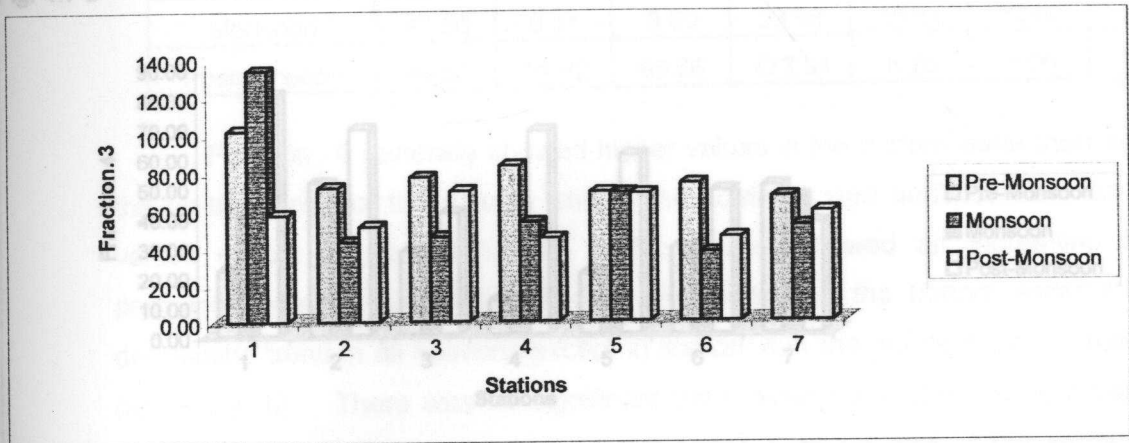
Fig: 4.6 a

Fig: 4.6 b

Fig: 4.6 c

Fig: 4.7 a

Fig: 4.7 b

Fig: 4.7 c

during premonsoon and postmonsoon in the north and postmonsoon in the south showed an increasing trend. In the premonsoon bottom water indicated an increasing trend in the northern part towards downstream and in postmonsoon a decreasing trend was showed in the southern part (fig 4.8 a, b) the sediment in the north showed a decreasing trend during premonsoon and an increasing trend in postmonsoon. An increasing trend was observed in the southern part during premonsoon and a decreasing trend in premonsoon (fig 4.8 c). The concentration of fraction.5 varied between 7 to 380.32 ng/l in the northern part and 3.63 to 384.55ng/l in the southern part of the estuary (Table 4.8 a). In the northern part fraction.5 concentration in the sediment varied between 3.24 to 173.04 ng/g and 2.58 to 90.44 ng/g in the southern part (Table 4.8 b).

Table 4.8.a. Fraction 5 in water (ng/l).
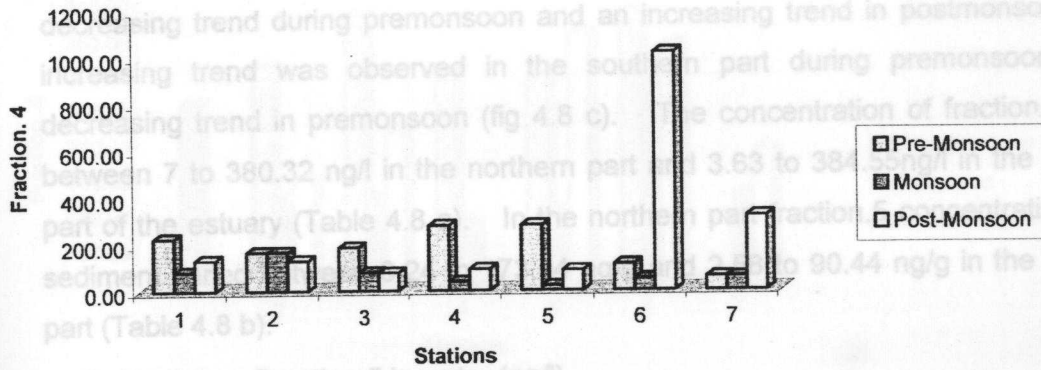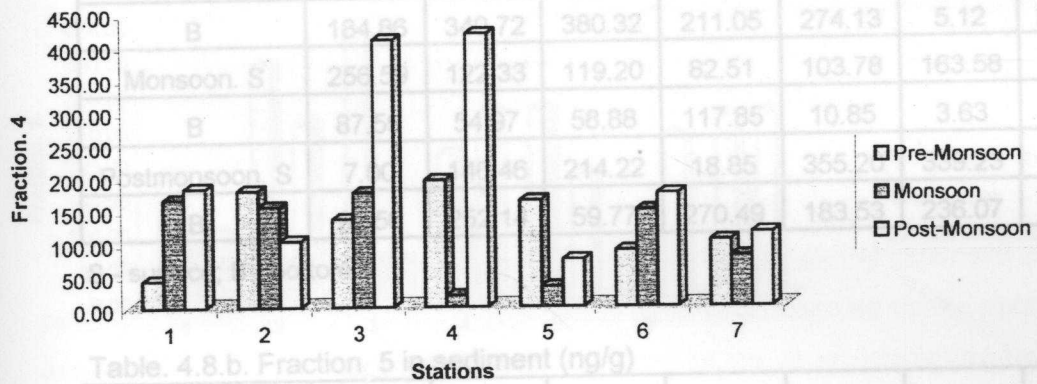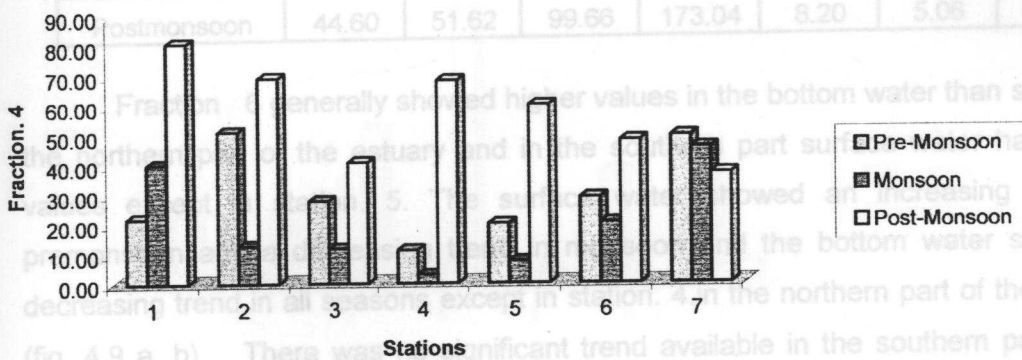
Station	1	2	3	4	5	6	7
Premonsoon. S	36.73	308.04	379.52	295.69	291.36	384.55	4.58
B	184.86	340.72	380.32	211.05	274.13	5.12	265.46
Monsoon. S	256.59	122.33	119.20	82.51	103.78	163.58	125.22
B	87.59	54.97	58.88	117.85	10.85	3.63	182.47
Postmonsoon. S	7.00	146.46	214.22	18.85	355.20	339.23	187.78
B	99.56	252.14	59.77	270.49	183.53	236.07	268.79

S - surface; B - bottom

Table. 4.8.b. Fraction. 5 in sediment (ng/g)

Station	1	2	3	4	5	6	7
Premonsoon	36.41	12.38	10.99	3.24	3.06	73.15	90.44
Monsoon	47.56	6.21	8.39	23.68	16.64	10.82	2.58
Postmonsoon	44.60	51.62	99.66	173.04	8.20	5.06	14.98

Fraction 6 generally showed higher values in the bottom water than surface in the northern part of the estuary and in the southern part surface water had higher values except in station. 5. The surface water showed an increasing trend in premonsoon and a decreasing trend in monsoon and the bottom water showed a decreasing trend in all seasons except in station. 4.in the northern part of the estuary (fig. 4.9 a, b). There was no significant trend available in the southern part of the estuary. The concentration of fraction.6 in the northern part of the estuary varied between 1.41 to 451.91 ng/l and 2.38 to 442.44 ng/l in the southern part (table 4.9 a). In the northern part of the estuary the sedimentary concentration showed minimum during monsoon and maximum in postmonsoon season. In the sediment, the

Fig: 4.8 a

Fig: 4.8 b

Fig: 4.8 c

premonsoon values showed a decreasing trend in the northern and southern part of the CES and an increasing trend in the southern part during postmonsoon season (fig 4.9 c). The concentration of fraction 6 varied between 3.72 to 198.58 ng/g in the northern part and 6.38 to 189.45 ng/g in the southern part (Table 4.9 b).
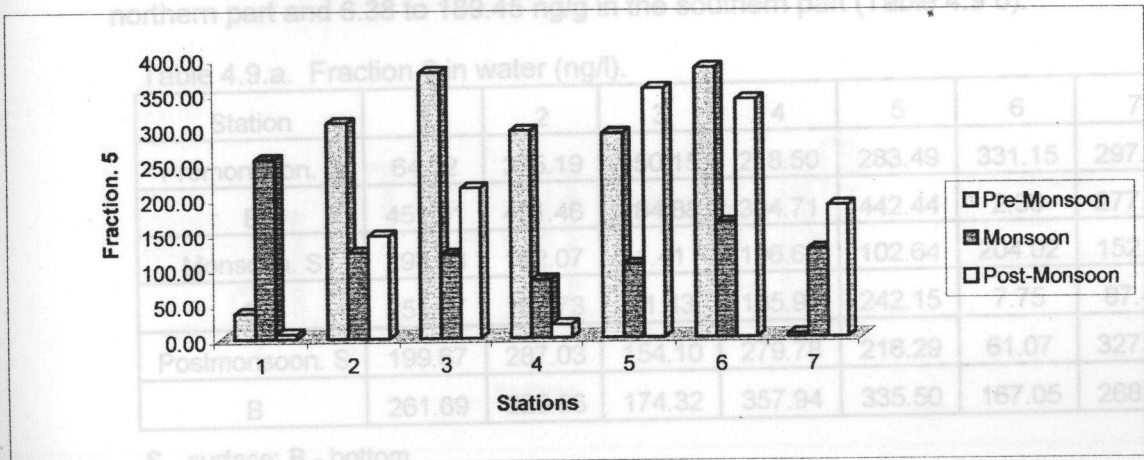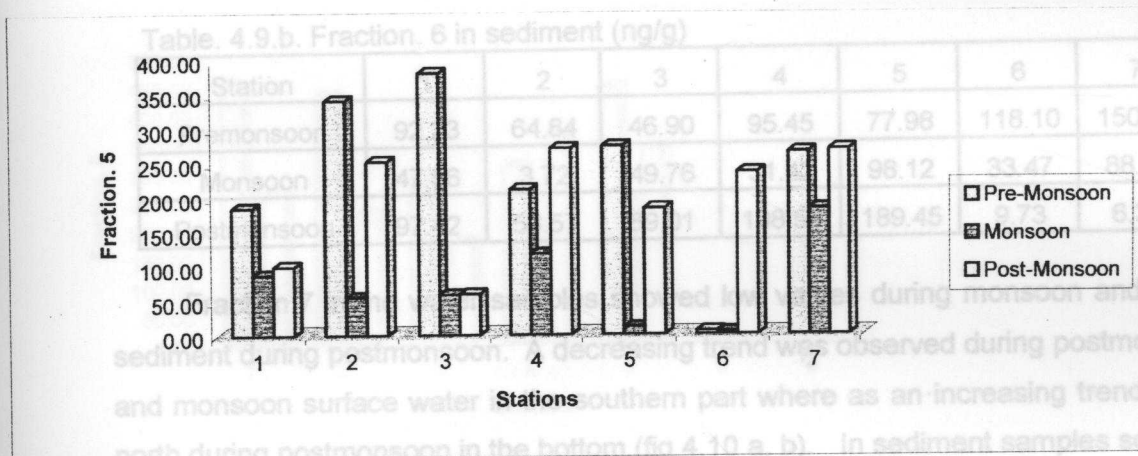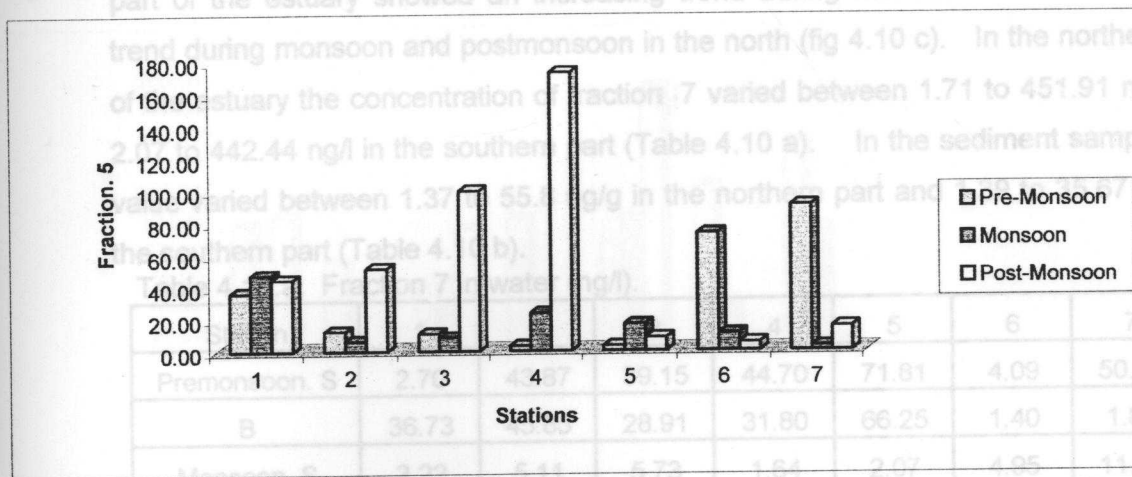
Table 4.9.a. Fraction 6 in water (ng/l).

Station	1	2	3	4	5	6	7
Premonsoon. S	64.12	375.19	450.15	218.50	283.49	331.15	297.85
B	451.91	431.46	284.88	304.71	442.44	2.36	277.62
Monsoon. S	293.28	162.07	1.41	196.67	102.64	204.02	152.12
B	251.37	162.73	91.43	185.97	242.15	7.75	87.42
Postmonsoon. S	199.67	287.03	154.10	279.78	216.29	61.07	327.74
B	261.69	225.96	174.32	357.94	335.50	167.05	268.51

S - surface; B - bottom

Table. 4.9.b. Fraction 6 in sediment (ng/g)

Station	1	2	3	4	5	6	7
Premonsoon	92.23	64.84	46.90	95.45	77.98	118.10	150.30
Monsoon	47.56	3.72	49.76	31.42	98.12	33.47	88.11
Postmonsoon	97.42	58.57	89.01	198.58	189.45	9.73	6.38

Fraction 7 in the water samples 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 (fig 4.10 a, b). In sediment samples southern part of the estuary showed an increasing trend during monsoon and a decreasing trend during monsoon and postmonsoon in the north (fig 4.10 c). In the northern part of the estuary the concentration of fraction 7 varied between 1.71 to 451.91 ng/l and 2.07 to 442.44 ng/l in the southern part (Table 4.10 a). In the sediment samples the value varied between 1.37 to 55.8 ng/g in the northern part and 1.39 to 35.67 ng/g in the southern part (Table 4.10 b).

Table 4.10.a. Fraction 7 in water (ng/l).

Station	1	2	3	4	5	6	7
Premonsoon. S	2.70	43.87	39.15	44.70	71.81	4.09	50.88
B	36.73	45.85	28.91	31.80	66.25	1.40	1.86
Monsoon. S	3.22	5.11	5.73	1.64	2.07	4.95	11.82
B	26.51	2.71	3.74	2.51	61.64	2.57	12.53
Postmonsoon. S	25.32	3.19	1.71	87.89	86.83	111.79	187.78
B	4.79	18.53	202.51	64.59	56.63	77.85	52.40

S - surface; B - bottom

Fig: 4.9 a

Fig: 4.9 b

Fig: 4.9 c

As the identity of the different fractions are not clear, no specific explanations for their distribution and seasonal character can be offered, but the following general observations.

(1). The relative concentrations of the fractions indicate a differential distribution pattern with a preferential higher level of some of these fractions. For e.g. in water fraction 6 is having a higher concentration than the rest.

(2). In seasonal distribution the following trend was observed in water.

 (a). In monsoon, fraction 5 (293.28ng/l in station. 1) having the highest concentration in the northern part and fraction. 6 (242.15 ng/l in station. 5) in the south.

 (b). In premonsoon, fraction. 6 (442.44 ng/l in station. 5) having the highest concentration in the northern part and fraction. 6 (1018.31 ng/l in station.1) in the south.

 (c). In postmonsoon, fraction 5 (287.53 ng/l in station 2) having the highest concentration in the northern part and fraction 4 (1018.31 ng/l in station 6) in the south.

(3). In sediment the seasonal trends are,

 (a). In monsoon, fraction 3 (133.47 ng/g in station.1) having the highest concentration in the northern part and fraction 2 (308.95 ng/g in station 7) in the south.

 (b). In premonsoon, fraction 3 (101.72 ng/g in station 1) having the highest concentration in the northern part and fraction 6 (159.2 ng/g in station 7) in the south.

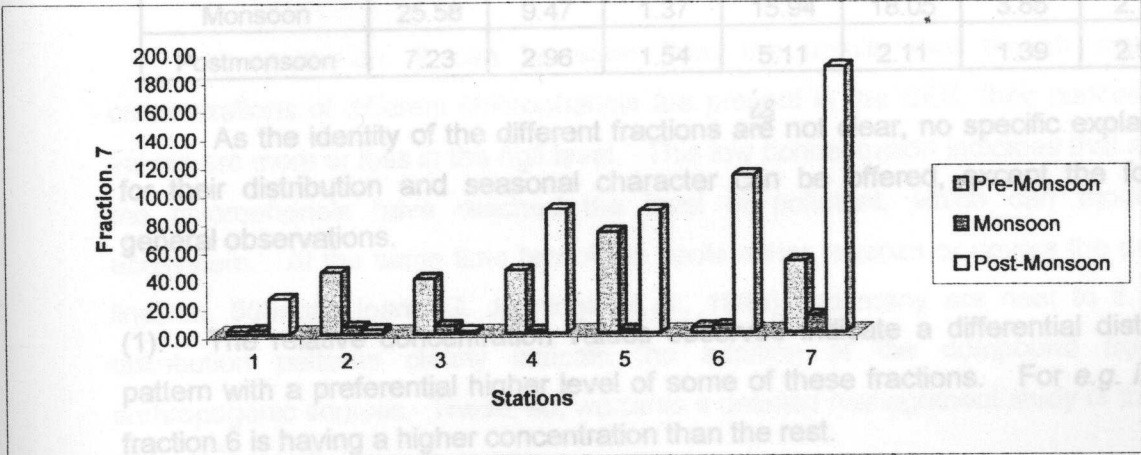 (c). In postmonsoon, fraction 4 (189.33 ng/g in station 4) having the highest concentration in the northern part and fraction 6 (189.45ng/g in station 5) in the south.
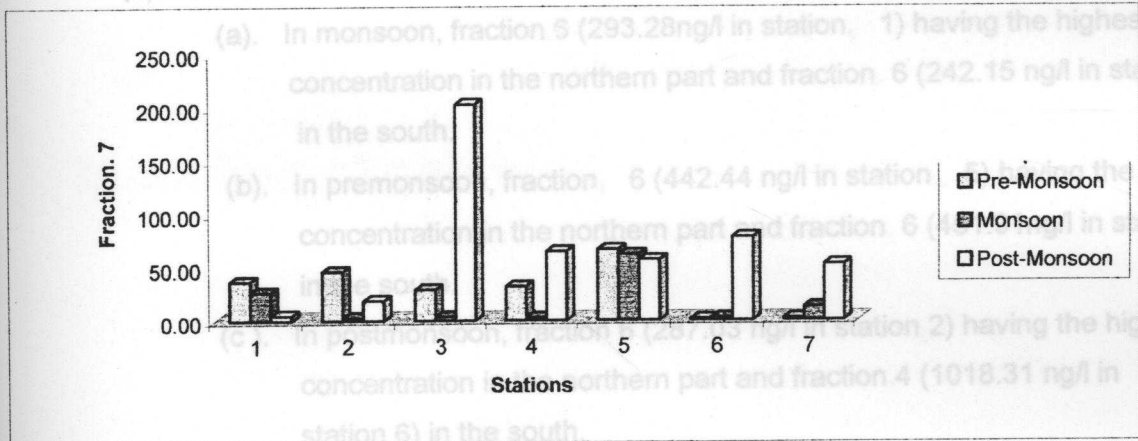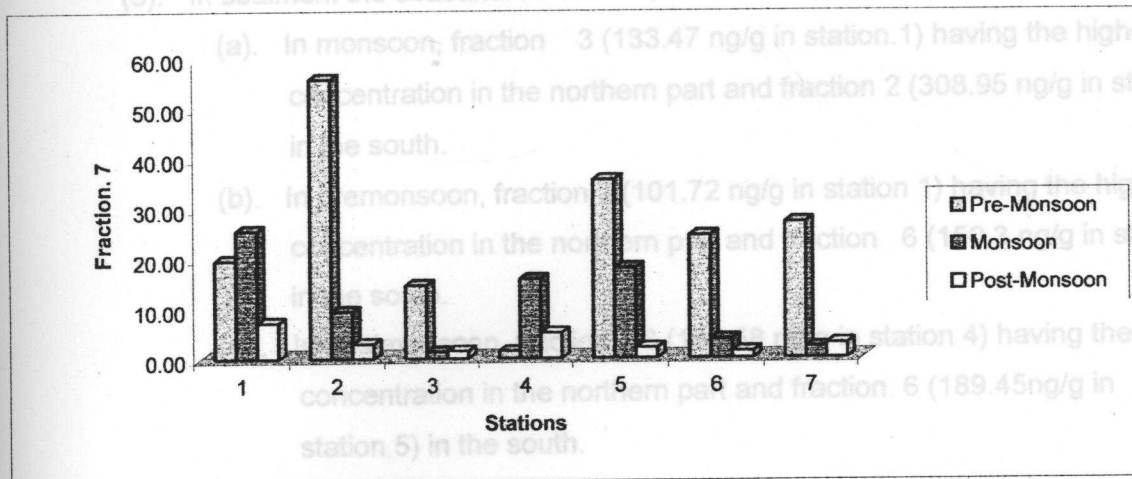
(4). No common trend can be assigned to the fractions, individual variations in distribution pattern prevails. At the same time, the general observation was that distribution of any fraction in the sediment exhibited either a trend opposite to that

Fig: 4.10 a

Fig: 4.10 b

Fig: 4.10 c

Table. 4.10.b. Fraction, 7 in sediment (ng/g)

Station	1	2	3	4	5	6	7
Premonsoon	19.67	55.80	14.73	1.54	35.67	24.51	27.13
Monsoon	25.58	9.47	1.37	15.94	18.05	3.85	2.18
Postmonsoon	7.23	2.96	1.54	5.11	2.11	1.39	2.95

As the identity of the different fractions are not clear, no specific explanations for their distribution and seasonal character can be offered, except the following general observations.

(1).   The relative concentration values observed indicate a differential distribution pattern with a preferential higher level of some of these fractions.   For e.g. in water fraction 6 is having a higher concentration than the rest.

(2).   In seasonal distribution the following trend was observed in water.

(a).   In monsoon, fraction 6 (293.28ng/l in station 1) having the highest concentration in the northern part and fraction 6 (242.15 ng/l in station 5) in the south.

(b).   In premonsoon, fraction 6 (442.44 ng/l in station 5) having the highest concentration in the northern part and fraction 6 (451.91ng/l in station.1) in the south.

(c).   In postmonsoon, fraction 6 (287.03 ng/l in station 2) having the highest concentration in the northern part and fraction 4 (1018.31 ng/l in station 6) in the south.

(3).   In sediment the seasonal trends are,

(a).   In monsoon, fraction 3 (133.47 ng/g in station.1) having the highest concentration in the northern part and fraction 2 (308.95 ng/g in station 7) in the south.

(b).   In premonsoon, fraction 3 (101.72 ng/g in station 1) having the highest concentration in the northern part and fraction 6 (150.3 ng/g in station 7) in the south.

(c).   In postmonsoon, fraction 6 (198.58 ng/g in station 4) having the highest concentration in the northern part and fraction 6 (189.45ng/g in station 5) in the south.

(4).   No common trend can be assigned to the fractions, individual variations in distribution pattern prevails.   At the same time, the general observation was that distribution of any fraction in the sediment exhibited either a trend opposite to that

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observed in water or no trend was shown. This can be attributed to the close relationship between the concentration of chlorophenols in water and sediment. The low reactivity of chlorophenols along with the common origin can be the major reason.

In conclusion, it can be seen from the results that though significant concentrations of different chlorophenols are present in the CES, their concentration values are more or less in the ng/l level. This low concentration indicates that none of the chlorophenols have reached the level of pollutant, which can modify the ecosystem. At the same time few of the spots either reaches or covers the pollution line, i.e. 500ng/l (Joane G. Jennings *et al.,* 1996) and many are near to it. The distribution patterns clearly indicate the addition of the compound from the anthropogenic sources. These, so, warrants a detailed management study of the CES with respect to these compounds.

Chapter 5

Modeling of chemical parameters in the CES