Chapter 5

Trace metals

5.1 Introduction

Of the chemical elements, metals make up the largest group; their characteristics, however, differ greatly within the biosphere. Heavy metals are common pollutants in urban aquatic environments, and in contrast to most other pollutants, are not biodegradable and are thus persistent in the environment. Many metals, a number of which are non-essential to plant and animal metabolism, are often toxic in low concentrations (Baker, 1981). But some other metals, in trace quantities, regulate the physiological processes and decide the health of the system. Thus, metals form an integral part of the aquatic systems and no scientific investigation on such systems would be complete without an assessment of metal interactions.

Both essential and non-essential metals were selected for the study in the three major phases of occurrence; dissolved, particulate and sedimentary. The essential metals comprise of iron, manganese, zinc, copper and cobalt and non-essential metals form another group comprising of chromium, nickel, cadmium and lead.

The respiratory pigment-haemoglobin, found in vertebrates and many invertebrates contain iron, while the respiratory pigment of many molluscs and higher crustaceans, haemocyanin, contains copper. Zinc is the element present in many proteinaceous enzymes. One of the important Vitamins, Vit.\(B_12\) contains cobalt. The second category, the non-essential metals are generally not required for metabolic activities and are toxic to the cell at quite low concentrations.

5.2 Dissolved trace metals

The most obvious medium of pollution assessment is the surface water of any aquatic system. The tendency and rate by which a metal participate in geochemical or biological process depends on the physicochemical forms in which that metal occurs in dissolved state in an aquatic environment. Information
emerging from recent studies strongly suggests that the chemical parameters controlling metal-organism interactions are the activities of free metal ions. If a metal exceeds the critical solubility limit in seawater, it may precipitate as a solid phase or adsorb on particulates and settle to the sediments. The residing biota can bioaccumulate metals from water and release it to the water on degradation of detrital biogenic matter. Generally, the concentration of total dissolved metal in aquatic systems are very low, yet they can be considered as the most important form for the aquatic organisms.

Iron

Iron is the most important biological and geochemical trace metal in the marine environment. It is an essential micronutrient for phytoplankton growth as an important component of such biochemical processes as photosynthetic and respiratory electron transport, nitrate and nitrite reduction, chlorophyll synthesis and a number of other biosynthetic reactions (Weinberg, 1989).

Iron in the present study recorded a maximum value of 260.30 μg/l at station 3 and a minimum of 25.60 μg/l at the reference station. From the monthly data (Table A.31), it can be seen that station 3 dominated in Fe content in almost all months. The annual average also was highest at this station, while the estuarine station showed the lowest concentration. Iron varied from 34.05 to 217.69 μg/l in the mangrove habitats, from 26.60 to 260.30 μg/l at station 3, and from 25.60 to 115.33 μg/l at the reference site (station R).

![Figure 5.1: Seasonal mean variation of dissolved iron](image)
Seasonal variation in Fe was quite unique for each sampling site (Figure 5.1). Station 1, Mangalavanam, which is a mangrove station showed lower values in the monsoon period whereas the ‘Fisheries’ station (station 2), which is a mangrove nursery showed lowest concentration in the premonsoon season. The riverine site recorded minimum value during monsoon period while the estuarine site exhibited a premonsoon minimum similar to the Fisheries station.

Chemical behaviour of iron and its solubility in water strongly depend on the oxidation intensity of the system in which it occurs, pH has a strong influence as well. The availability of iron in aqueous solution is greatly affected by environmental conditions, especially changes in degree of oxidation and reduction. Fe is present in plant debris and organic wastes in soils and the activities in the biosphere may also have a decisive role on the occurrence of Fe in water. Microorganisms are commonly involved in processes of oxidation and reduction of Fe, since some species may use these reactions as their energy source. Higher concentration of dissolved ferrous iron can occur at the site of either reduction of ferric oxyhydroxides or oxidation of ferrous sulphate. In the latter process, if sulphur is attacked first and altered to sulphate, ferrous iron is released. Kremling (1983) has pointed out that considerable change in the abundance of Fe and Mn will occur across the redoxcline i.e., H₂S - O₂ interface.

In the mangrove ecosystem, trace metals can enter with incoming tide associated with suspended particles and Fe and Mn oxyhydroxides (Lacerda et al., 1998). When reaching the reducing condition dominant in most mangroves, these oxyhydroxides are reduced and dissolved and can release their trace metal load into the water column (Lacerda et al., 1999). In the anoxic waters, the Fe (III) oxide/hydroxide is transformed to Fe (II) sulphides. Some iron is dissolved as ferrous iron and iron sulphide complexes (Kremling, 1983). In this peculiar environment, enormous load of organic matter is the reason for the permanent anoxic condition. Most of the contaminants tend to be adsorbed onto suspended particles and removed from water column to the sediments (Bourg, 1988; Millward and Turner, 1995) although redox sensitive elements like Fe with great affinity for organic matter can be intensively remobilised during the early degradation of settling organic matter (Froelich et al., 1979; Berner, 1980). These mechanisms may be the reason for the elevated levels of dissolved Fe in the mangroves.
Moreover, many authors have opined that benthic flux is enhanced by the high content of fine-grained fraction with high levels of organic matter in the sediments (Aller and Beninger, 1981; Irion and Muller, 1990). Apart from this remineralization of organic rich particles, enrichment of dissolved Fe may have resulted in the present study from reductive dissolution of solid Fe from within the sediment and transported to the water column.

Seasonally, postmonsoon recorded the highest value. Desorption of Fe from particulate matter facilitated by the long residence time of the particles in the water column during this period may be the reason for the elevated concentration. Lower values observed at station 1 during monsoon may be due to the dilution of the metal by the heavy monsoon rainfall coupled with land run-off. However, such a monsoon minimum was not exhibited by station 2. Here, the lowest concentration was observed in the premonsoon period. At this particular site, water level was low in the creek waters during monsoon because the entrance for floodwaters was closed in order to prevent the escape of prawn larvae. Hence, in this stagnant condition, diffusion of trace metals from the sediments is highly favoured resulting in a monsoon-associated concentration hike. Of the two mangroves, the Fisheries station (station 2) exhibited higher annual mean concentration. Reduction of oxygen in sediments through biologically catalyzed processes is piloted by high load of organic materials and water stagnation due to low tidal activity may be the reasons for the observed behaviour. Thus, the higher dissolved Fe concentration in these two mangrove stations compared with the estuary suggests that there is an important release of dissolved Fe from the sediment-water interface which is possibly due to reduction of iron oxides by bacteria during the mineralization of organic carbon.

The dynamics of heavy metals are often more complicated in rivers and streams than in lakes and oceans. In most rivers, the dissolved fraction contains the most active form, colloids. All the colloids in aquatic systems are coated with natural organic matter and this organic coating is the main reason why these natural colloids are negatively charged and very reactive to heavy metals (Beckett, R., 1990; Murray and Gill, 1978; Hong and Kester, 1985; Tripping, 1986; Tripping and Cooke, 1982). Fe has an extensive ability to form complexes with naturally
occurring organic compounds. Besides, Fe occurs in high concentration in river water than in seawater.

The relatively high concentration of dissolved Fe in the riverine station can be related to the prevailing pH of that system. In the low pH, Fe present will be mostly in the soluble Fe$^{2+}$ oxidation state. Influence of pH on Fe distribution was also reported by Aston and Chester (1973). The effluents from the nearby industries are the major contributors of heavy metals into this system. The elevated levels of Fe observed in the premonsoon period can be attributed to the reductive dissolution of solid Fe from within the sediment and transported to the water column facilitated by the reduced flow regime characteristic of this season. Considerable dilution may have occurred causing a reduction in the dissolved Fe in the monsoon season. Colloidal Fe, which, can pass through 0.45μm filter can be another source for Fe at this site. Lack of correlation with any of the hydrographical parameters (Table C.2) emphasizes the role of anthropogenic input in the distribution of Fe at this station.

In the present study, a significant negative correlation of Fe with salinity was observed in the estuary (Table C.2). This non-conservative behaviour of Fe is reported in other estuaries also (Wu and Luther, 1995, 1996; Luther and Wu, 1997; Johnson et al., 1999). The inverse relationship with salinity shows that processes determining Fe distribution may include fresh water source of Fe, Fe removal by particle scavenging and phytoplankton uptake, sedimentary Fe input and atmospheric deposition. In estuaries, Sholkovitz (1976) and Boyle et al. (1977) suggested a physical association of colloidal humic acids and colloidal Fe-OH. Simple co-removal of humic acids and Fe may be all that is seen with an increase in salinity as the colloids become destabilized and flocculate (Eastman and Church, 1983). In the estuary, due to high tidal activity, intrusion of seawater impoverished in metal content may dilute the estuarine water causing a reduced soluble Fe levels at this site compared to other systems. Furthermore, the increased amount of sea salts can remove the soluble Fe from the water column. Ouseph (1992) has pointed out that the chief source of Fe in the Cochin estuary is the land drainage, harbour activity and sewage. The concentration levels observed in the present study fall within the range observed in the same and neighbouring aquatic systems (Joseph, 2002; Unnikrishnan, 2001; Shibu, 1992; Ouseph, 1992).
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Manganese

The chemistry of manganese resembles that of iron in that both metals are redox sensitive and are relatively mobile in the aquatic environment. The thermodynamically stable form of manganese in oxic seawater is Mn (IV). The nitrate, chloride and sulphate salts of Mn are soluble in water, whereas, the corresponding hydroxide, sulphide, carbonate, oxide and phosphate salts are sparingly soluble and are removed in the particulate fraction from the water column (Luther et al., 1986).

Dissolved Mn concentration in the study area varied between 3.060 and 244.7 μg/l in the mangrove stations, from 3.20 to 20.710 μg/l in the polluted river site and from 4.620 to 21.16 μg/l in the estuary (Table A.32). Mangrove stations showed highest annual mean concentrations while the estuarine and riverine sites recorded comparable concentrations. Seasonally, premonsoon season was characterized by the dissolved Mn hike in both mangrove sites with monsoon season exhibiting the minimum (Figure 5.2). However, monsoon period recorded the maximum concentration in the riverine and estuarine sites.

Manganese Sulphides are very unstable ($K_{sp}$ (MnS) = 9.6 and 12.6) (Forstner and Wittman, 1979) and are only formed when total dissolved S exceeds total carbonates by a factor of at least 100 (Krauskopf, 1979). Therefore, manganese sulphides have never been detected in mangroves (Lacerda et al., 1998). Under the prevailing anoxic conditions, many bacteria that can oxidize organic matter, with
the reduction of Fe (II) can also reduce Mn (IV) in a dissimilatory fashion using it as an electron acceptor. Also, under the anoxic condition, Mn (IV) is easily reduced through non-enzymatic mechanisms to soluble Mn (II) (Graton et al., 1990; Lovely, 1993; Sprat et al., 1994; Luther (III) et al., 1998). Thus, Mn would not behave like most other trace metals and a significant fraction of this element is available for plants. However, these mechanisms would also make Mn available for exportation to adjacent coastal waters. Another significant source of Mn is the freshly formed manganese coated particles entering the mangroves from nearby estuarine waters. On entering the reduced condition during the ebb tide inside the mangroves, these Mn coatings dissolve releasing soluble manganese.

The intense low redox potential of the mangrove sediments facilitates the remobilization of this element in the mangroves. The diffusive input from the sediment–water interface and pore waters are yet another source for this metal in this environment. Many authors have emphasized the importance of benthic input of this metal resulting in elevated dissolved fraction in many water bodies (Santchi et al., 1990; Morris et al., 1982; Davison, 1993).

The seasonal trend showed a hike in concentration during premonsoon period at the mangrove sites. Warmer temperature, characteristic of this season would have resulted in enhanced bacterial activity, which, in turn, facilitates the release of soluble Mn to the water column. Furthermore, a significant positive correlation between dissolved Mn and temperature (Table C.2) was observed supporting the argument. This covariance of temperature and dissolved Mn confirms the temperature driven effect on distribution of this metal. Most likely, the balance between oxidation and reduction rates determines Mn concentration. Monsoon dilution by the heavy influx of fresh water may explain the lower values observed in this season. Dissolved Mn concentration in the South East Brazilian mangroves were in the range 2.8μg/l – 26.10μg/l (Lacerda et al., 1999). In this study, the summer concentration values of soluble Mn were much higher than the winter concentration levels. Except the peak value in April, the concentrations reported in the present study are in the range of that in the Brazilian mangroves.

Very high levels of soluble Mn in rivers are reported elsewhere (Morris et al., 1982, Davison, 1993). Seasonal variation in Mn, Fe, Zn and Pb may be
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controlled by the redox condition of the river basin (Shiller, 1997). In the present study, monsoon season showed slightly higher values with the non-monsoon months with similar values at station 3. The monsoon maximum can be related to the land run-off coupled with the effluents from the nearby industries. According to Iwashita and Shimamura (2003), reducing conditions can occur in bottom waters of stratified lakes or reservoirs, riverbed sediments and stagnant streams. In the non-monsoon period, inflow is greatly reduced and the residence time of particulate and finely suspended sediments in the water column is increased. This facilitates the desorption process to occur and reduced conditions, which may be developed in the surface sediments greatly favours the migration of soluble form into the overlying water. Such an enhancement in concentration in the post and premonsoon may explain the low seasonal variability at this station.

None of the hydrographical parameters exerted any influence on metal distribution at this site (Table C.2). Lack of correlation with salinity and pH may be due to the narrow salinity range observed in this area. Fe and Mn are commonly associated with particles (Figueres et al., 1978; Rue and Bruland, 1995) and, therefore, the independence of concentration of Fe and Mn with salinity in Chitrapuzha is probably due to inputs from sediments. In addition to this the non-correlation points to the anthropogenic perturbations taking place in this area.

Dissolved oxygen values were found to be higher in this riverine station. In the oxygenated waters Mn would remain preferably in the +4 oxidation state, which is insoluble in water. This oxidized form of Mn is found to be associated with particulate matter in the form of oxyhydroxides. This may explain the lower concentration of dissolved Mn in the river station compared to the mangroves. Sokolowski et al. (2001) reported annual dissolved Mn concentration of 15.3μg/l in the Vistula River whereas in the Terminos fresh water lagoon the levels were much higher (0.002-0.118mg/l) (Vazquez et al., 1999). In a study by Joseph (2002) in the same river, the concentrations were in the range of that in the present study.

Factors affecting the hydrogeochemistry of Mn in estuarine waters are different from the rest of the water bodies selected for the study. Here, the prime hydrographical parameters such as salinity and temperature exhibited an inverse relationship with dissolved Mn (Table C.2). Mn is a highly reactive element and
dissolved Mn concentrations are low in oxic waters as a result of oxidative scavenging onto suspended particles. Reduced Mn species oxidize to insoluble manganese oxyhydroxides as amorphous coatings, frequently associated with iron (Giblin et al., 1986; Saager et al., 1997). The freshly formed Mn coatings are very efficient in scavenging additional manganese and iron, as well as other trace metals from the water column. This partly explains the inverse relationship with salinity. Studies done by Laslett and Balls (1995), Owens et al (1997), Morris and Bale (1979) also reported a non-conservative nature of Mn, with positive deviation from the theoretical mixing curve at low salinities and removal at higher salinities.

Monsoon peak in concentration exhibited at this station can be due to increased run-off from land, which is rich in Mn containing particles, desorption from suspended particles (Bewers and Yeates, 1978), reductive solubilization (Duinker et al., 1979; Laslett, 1995) and advective and diffusive fluxes of sediment pore waters (Morris and Bale, 1979; Kox et al., 1981; Laslett, 1995). A similar distribution pattern was reported in the Cochin Estuary also (Joseph, 2002; Ouseph, 1992; Sankaranarayan and Rosamma, 1978; Babukutty and Chacko, 1995; Shibu, 1992). Kayamkulam estuary, which is also a part of the Vembanad estuary, showed similar behaviour though concentration was much higher (Unnikrishnan, 2000). Studies done elsewhere showed higher concentration than the present study (Mzimela et al., 2003; Bucciarelli et al., 2001; Hatje et al., 2003; Gavis and Grant, 1986). However, in a study on Lake Tanganyika, Chale (2002) reported similar concentration values. The lower values recorded at the estuarine site in the present study can be attributed to its geographic disposition. The regular tidal activity brings in seawater impoverished in trace metal during each flood period. Considerable dilution together with increased sorption aided by the high saline waters favours the depletion of soluble Mn from the water column.

> Zinc

Zinc is a heavy metal, which is able to exert acute and chronic toxic effects in a range of fauna and flora. It is also able to bioaccumulate and thereby poses a potential threat to the food chain.

Dissolved zinc showed peak values at station 1, the mangrove site. The order of annual mean concentration of the sites are, station 1 > station 2 > station 3 >
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The two mangrove stations recorded high concentrations during postmonsoon period, while, station 3 and station R showed peak values in monsoon season (Figure 5.3). Significantly high concentration of Zn was observed in the months October and November at station 1. Concentration of Zn in the mangroves ranged from 32.90-111 µg/l at station 1 and from 24-88.25 µg/l at station 2. Station 3, showed wide variation in concentration (8.575–86 µg/l); while station R, the estuarine site, recorded Zn in the range, 7.75–28.75 µg/l (Table A.33). ANOVA calculation showed highly significant variation between stations (Table B.6).

![Figure 5.3: Seasonal mean variation of zinc](image)

The wide variation in the concentration of dissolved zinc at the mangrove stations can be partly due to the anthropogenic activities. Petroleum hydrocarbons were reported from station 1 in earlier studies. In addition to this, the peculiar reducing environment dominant in the mangroves regulates the dissolved zinc distribution. Pore water diffusion is particularly favoured due to the anoxic condition of the mangrove sediments. Zn, like Cu, is found to have a high complexing capacity with dissolved organic carbon (Mattheisson et al., 1999). The dissolved organic matter abundant in the creek waters might have favoured the presence of Zn in the dissolved state. Zn showed a highly significant negative correlation with pH at station 1 (Table C.2). This type of correlation was noticed by Grande et al. (2003) in the Tinto Odiel estuary in Spain. They attributed this to the tidal flushing, which in turn, cause an increase in pH. This results in the precipitation of metals that are no longer soluble and eventually concentrate in the sediments. The elevated levels of Zn and Cu in the non-monsoon period in the mangroves can be attributed to the concentration by evaporation and increased
dissolution from sediments due to high temperature and large contact time in summer (Paul and Pillai, 1983). The warmer temperature can lead to intense bacterial activity releasing high trace metal load into the water column by diagenetic processes. In fact, Zn concentration was found to co-vary with nitrate at station 1 (Table C.11). Since nutrient releases are due to remineralization of organic detritus by microbial activity, it would appear that Zn might have been released by the same process. Church (1986) and Windom et al. (1988) observed similar relationships between cadmium and phosphate in the Delaware estuary and between zinc and nitrate in the Bang Pakong estuary and reached similar conclusions.

Zn can have a large riverine source. The fine suspended sediments of the rivers are associated with large quantity of Zn (Stevenson and Betty, 1999; Sokolowski et al., 2001). The process of removal (desorption) from particles might be an important factor responsible for the presence of soluble Zn at the riverine site in the present study. Seasonally, Zinc showed remarkably high monsoon concentration. This can be related to the land run off and influx of metal-rich freshwater. The increased particulate matter load along with suspended sediments brought in by the streams would also be a possible reason for the abnormally high values in monsoon season. The runoff water may contain discharges from the agricultural area containing fertilizer, pesticides and rhodenticides. The effluents from the nearby industries may be the most probable source of this metal. A significant quantity of Zn may have been present in the effluents and the monsoon showers augment its release from the sediments. Senthilnathan and Balasubramanian (1999) observed a similar distribution pattern in the Pondicherry Harbour waters and attributed the summer minima to the utilization and uptake of Zn along with nutrients by residing biota. A similar distribution pattern and concentration range was reported in a previous study by Joseph (2001). Subarnarekha River, one of the polluted rivers of India, recorded higher values for dissolved zinc both in the monsoon and premonsoon seasons (Senapati and Sahu, 1996). Ouseph (1992) observed the zinc concentration in Periyar, one of the major rivers draining into Cochin estuary, to be in the range 24-65 μg/l. This value is higher than that observed in the present study.
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There is much published information on the presence, speciation and partitioning of Zn in estuarine waters (Elbaz-Poulichet et al., 1996; Comber et al., 1995; Ouseph, 1992; Lazlett and Balls, 1995; Flagel and Sanudo-Wilhelmy, 1993; Boughriet et al., 1993; Harper, 1991). Dissolved Zn varied between 7.750µg/l and 28.750µg/l in the estuarine station in this study. The concentration was much less than those of the mangroves. Seasonally, monsoon recorded the maximum and postmonsoon the minimum concentration. This site behaved similar to the riverine site. The monsoon hike can be the result of land runoff and influx of metal-rich freshwater. The suspended sediments and particulate load of the rivers draining to this estuary are considerably increased during this season causing a subsequent increase in the dissolved metal content. Warnken (2001) has pointed out that other than inputs from rivers, inputs from sediments by diffusive, bioturbative and bio-irrigative processes contribute to the estuarine Zn load. Pore water intrusion may account for part of the observed high levels of dissolved zinc during premonsoon period compared to the postmonsoon season, especially in the anoxic sediments. Since, mobile bed sediment is enriched in trace metals compared with suspended particulate matter, the principal source of dissolved metal may be the desorption from fine, re-suspended bed particles, possibly augmented by metal bearing sedimentary organic matter (Martino et al., 2002). Besides, Windom et al. (1988) have shown that the dissolved concentration of Zn increased due to degradation of sediments or suspended particulate organic matter. Other sources of Zn in the estuary may be intense boat traffic. The sacrificial anodes used in boats are a significant source of Zn to the water (Mattheisson, 1999).

The concentration levels in the premonsoon season were higher than in the postmonsoon season at the estuarine site. This may be due to desorption of Zn from particles at higher salinities. The tendency of dissolved Zn to resist removal during estuarine mixing has been noticed by Nair et al. (1990) and Shibu et al. (1990) in the northern part of the Cochin estuarine system and in other estuaries (Dunker, 1980; Eaton, 1979; Danielsson et al., 1983; Windom et al., 1988). But this observation is in contrast to the previous work done by Ouseph (1992) in the Cochin estuary itself. However, in a recent study, Joseph (2001) observed a similar monsoon maximum. The concentration levels recorded in the present study is within the range reported for other Indian estuaries (Govindsamy and Azariah,
1999; Senthilnathan and Balasubramanian, 1997; Subramanyan and Ananthalakshmi Kumari, 1991; Satyanarayana et al., 1990; Joseph, 2001; Shibu, 1992; Babukutty, 1991) but are lower than the estuaries in other parts of the world (Mzimela et al., 2003; Mattheissen et al., 1991; Carrasco et al., 2003; Stevenson and Betty, 1999; Velasquez et al., 2002; Baeyens et al., 1998).

**Copper**

Copper is an essential metal for all biological life, but is toxic at higher concentration, especially in the early developmental stage of many organisms (Spear and Pierce, 1979). Copper is found to preferentially adsorb to organic matter (Davis, 1984). Particle bound and organic complex bound copper reduces the reactivity and hence its toxicity (Engal et al., 1981; Apte et al., 1990; Gardner and Ravenscroft, 1991). The reactivity will depend on both the chemical and physical environment to which Cu is introduced.

![Figure 5.4: Seasonal mean variation of dissolved copper](image)

Dissolved copper varied from 1-16.9 µg/l in the mangroves, from 4.1 to 14.5 µg/l in the river Chitrapuzha and from 2.3 to 17.6 µg/l at the estuarine station (Table A.34). Seasonal mean variation of dissolved copper is depicted in Figure 5.4. In the mangroves as well as in the river, premonsoon period was characterized by the highest dissolved copper concentration. At stations 1 and 3, monsoon recorded the minimum, whereas, at station 2, postmonsoon season exhibited the minimum. The estuary showed a completely different picture with a monsoon hike and premonsoon minimum. ANOVA calculations showed a significant variation within months but not within season or stations (Table B.6). Highest annual mean
concentration was observed at station 2, while the lowest concentration was recorded at station 3.

In the mangrove stations Cu was found to co-vary with salinity (Table C.2)). This positive correlation with salinity indicates that variables other than salinity is controlling the metal levels in this system (Vazquez et al., 1999). Processes such as mobilization and removal can control total metal concentration in these mangroves. Shallow depth of the mangrove promotes the resuspension of sediment by tidal action. This activity encourages the release of soluble Cu from the sediments to the water column. The reducing condition of the mangroves remarkably favours pore water diffusion of Cu into the overlying water. In a pore water metal content study, it was shown that interstitial water of the top few centimeters of the core are enriched in Cu content than the rest of the core (Joseph, 2001). This finding again confirms the reductive dissolution of copper from the sediments. Redox sensitive elements such as Fe and Mn were found to present in great concentration in this study. Scavenging action of these metals also control distribution of other elements like Cu, Zn etc. Some organisms are known to concentrate significant amounts of Cu. Relatively high concentration of the element in the mangroves may be due to its release from organisms during their decomposition.

Only a small amount of Cu is associated with particulate matter. Bulk of the metal stays complexed, probably with humic substances as Cu has a strong binding strength to humic substances. According to Irving-Williams series, only Hg exceeds Cu in affinity to humic substances (Chester, 1990). In these mangroves, humic substances were detected in great amounts (Rini, 2002). The inverse relationship with pH (Table C.2) can be related to the tidal activity. The tides chlorinate and increase the pH of the system. This sudden increase of pH results in the precipitation of metals that are no longer soluble and concentrate in the sediment (Borrego, 1992; Borrego et al., 2001; Braungardt, et al., 1998; Grande et al., 2000; Sainz et al., 2002). According to Shiller and Boyle (1985), pH gradient could influence the solubility through acid-base reactions or through the influence of pH on the adsorption-desorption of trace metals and redox reactions.

General distribution of dissolved Cu in the river very much resembled the mangroves. Copper is used as a catalyst in many industrial processes, which might
have led to large inputs of anthropogenic copper into the river. Moreover, the two main components in river water discharge are minerals and organic matter and both of them are identified as the main carriers of copper to the watershed (Bergkvist et al., 1989).

The premonsoon maximum at this station points to the strong association of copper with organic complexing agents such as humic and fulvic acids, which resist desorption even if sea salts concentration is increased (van den Berg et al., 1987; Muller, 1996, 1998). Mattheissen (1999) has shown that a proportion of dissolved Cu will probably have been adsorbed on colloidal particles, which would pass through 0.45μm filter. It is doubtful that materials adsorbed on to such particles are fully bioavailable, although, some fine particles are indeed able to bioaccumulate across cell membranes by pinocytosis, and copper can easily desorb from such particles under such conditions (Benoit et al., 1994; Windom et al., 1983). Since river water is rich in colloids, this desorption mechanism may be another source for dissolved copper in the summer season. Monsoon minima can be due to the dilution of the metal by the heavy influx of freshwater. A significant positive correlation with salinity and temperature further confirms this observation (Table C.2). In the Sagami river and tributaries temperature is found to be the factor determining the seasonal distribution (Iwashita and Shimamura, 2003). In the Subarnarekha River, Cu concentration was high in the premonsoon than in postmonsoon (Senapati and Sahu, 1996). Govindsamy and Azariah (1999) linked premonsoon maximum of Cu to the major source of metal pollution, intensive human activity, discharge of domestic as well as industrial effluents and municipal wastes. Further, higher concentrations of Cu, nitrate and phosphate were recorded at station 3 in the same season perhaps, as a result of organic matter decomposition. Significant positive correlations with nitrite and phosphate also point to this source (Table C.11).

Thus, the enhanced level of Cu in the non-monsoon period observed at the riverine and mangrove stations in this study can be related to the concentration of the metal by evaporation and increased dissolution from the sediments, due to the higher summer temperature and larger contact time of the particles.
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The distribution of Cu in the estuary was different from the remaining aquatic systems analyzed. Here, a monsoon maximum and a premonsoon minimum were seen. Significant negative correlations with salinity and temperature were also obtained (Table C.2). Interestingly, Cu showed strong correlations with dissolved Fe and Mn (Table C.8). This inverse relationship was noted by many authors (Martino et al., 2003; Riso et al., 1993; Sokolowski et al., 1999; Windom et al., 1983; Windom and Smith, 1985; Ouseph, 1992; Paul and Pillai, 1983; Senthilnathan and Balasubramaniam, 1997; Sholkovotz, 1976; Byrd et al., 1990; Flagel et al., 1991; Aller, 1994; Sanudo-Wilhelmy et al., 1996; Elbaz-Poulichet et al., 1987; Bayens et al., 1998; Garnham et al., 1991; Paalman et al., 1994; Schlekat et al., 1998). This relationship reveals that large quantity of Cu is removed from the water column and precipitated as suspended matter, which may contaminate the bottom sediment. This behaviour again showed contribution from fresh water sources and indicated that physical mixing is a significant factor in contributing the soluble Cu. In a study on estuaries of South East Coast of India, Senthilnathan and Balasubramaniam (1997) observed a decreasing nature of dissolved copper with increasing salinity and related this to the dilution of metal-rich river water by metal-impoverished seawater and to the rapid sedimentation occurring in estuaries. In addition, a sudden increase in salinity associated with sudden change in freshwater conditions in the summer months would result in the coagulation and precipitation of colloidal clay particles and co-precipitation of metal with/ or adsorption onto the particles and remove considerable amount of metal from solution. Thus the non-conservative behaviour can be attributed to the internal sources such as metal desorption from suspended particles, diagenetic remobilization from bottom sediments or anthropogenic inputs.

The monsoon maximum found at this estuarine site can be due to land run-off and influx of metal-rich freshwater. Monsoon-associated hike in dissolved copper has been observed in other Indian estuaries like Zuari, Uppanar, Vellar and Kaduviar. Uptake of Cu by biota is more pronounced during periods of low river flow when the flushing time is increased (Uncles et al., 1983), when increased river flow reduces the flushing time and adsorption onto particles is hindered by slow
kinetics (Millward et al., 1992). In the latter case, metals are more likely to be flushed from the estuary in the dissolved form.

Other possible source of Cu in this estuary would be the intense boat traffic. Cu is an efficient biocide and has been used in anti-fouling paints on boats. In a laboratory study by Valkirs et al. (2003), it was found that the Cu emission from anti-fouling agents could be a substantial portion of the total dissolved copper loading into a harbour or estuary. Approximately 70% of the estimated total annual Cu loading in the San Diego Bay originates from either leaching process or mechanical cleaning of anti fouling coatings. Cu was found to have a strong association with Fe and Mn in this study. This indicates that Cu occur in association with oxyhydroxides of Fe and Mn and desorption of these amorphous particles could increase the concentration of metals bound to them. A benthic flux of soluble Cu driven by aerobic degradation of sedimeted materials at the bottom enhanced by high content of fine-grained fraction with relatively high levels of organic matter in the sediments is also possible. A similar conclusion was reached by other researchers also (Tappin et al., 1995; Aller and Beninger, 1981; Irion and Muller, 1990).

\[ \text{Cobalt} \]

Cobalt, one of the biologically essential metal, showed a diverse distribution pattern in this study. ANOVA statistics revealed insignificant variation between stations and season (Table B.6). The annual mean concentration was highest at station 3. Of particular interest, one of the mangrove stations exhibited lowest annual mean concentration. At all stations except station 2, monsoon recorded the minimum value (Figure 5.5). Postmonsoon period was shown to have elevated concentrations at station 2 and 3, whereas station 1 and R were characterized by a premonsoon maximum. Cobalt varied from 0.050 to 1.330μg/l at the mangrove sites, while the riverine and estuarine sites recorded the element in the range 0.130 to 2.330μg/l and 0.170 to 3.900μg/l respectively (Table A.35).
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Figure 5.5:- Seasonal mean variation of dissolved cobalt

Among the mangroves, the Fisheries station exhibited higher concentration. This can be due to the intense reducing condition existing there. As the tidal activity is low limiting the possibility of influx of oxygenated estuarine water, anoxic condition was prominent in this area for longer periods of time throughout the year. Thus, pore water infusion is highly favoured in this environment. Brooks _et al._ (1968) and Presley _et al._ (1972) have shown that Co in the interstitial water is 2-5 fold higher than the overlying water. This higher concentration, in turn, showed that precipitation as sulphide does not control the dissolved metal concentration. Instead, mobilization takes place by the formation of metal complexes. Such a source of dissolved Co has been suggested by Martino _et al._ (2003), under reducing condition. The bacterial and chemical degradation of particulate organic matter and resuspended sediment formed by the intense bioturbation can further contribute to the soluble Co pool in this system.

At the ‘Fisheries’ station, Co showed highly significant positive correlations with Mn and Ni, whereas, only Fe exhibited a significant correlation with Co at station 1 (Table C.8). All these clearly show a common source for these metals, probably by the reductive dissolution of Fe and Mn oxides. Forstner and Wittman (1981) have observed desorption of Co from clay minerals and freshly precipitated Fe(OH)$_3$, when the minerals are brought into contact with seawater. The monsoon minimum indicates that considerable dilution took place during this period. Only station 2 showed minimum values in the premonsoon season. This may be due to the removal of substantial portion of the soluble metal from water by the biota and binding onto suspended particles. Since inflow of fresh water is considerably reduced
in this period, residence time of particles in the water column is increased causing an efficient readsoption of Co onto suspended particles. This re-adsorption mechanism was kinetically proven by Ciffroy (2003) in a laboratory study.

At the estuarine site as well as at station 1, dissolved Co showed a significant positive correlation with salinity (Table C.2). This confirms the desorption mechanism of Co with salinity changes. Several workers have noted this behaviour (Forstner, 1979; Ciffroy et al., 2003; Martino et al., 2002; Senapati and Sahu, 1999; Govindsamy and Azariah, 1999; Breuer et al., 1999). In a kinetic study on the sorption behaviour of metals, Dyressen and Kremling (1990) have shown that Co and Ni have the intermediate values of solubility values with Mn being most soluble and Cd the least. Thus, desorption mechanism is operative in the case of Co if the ionic strength of the solution vary accordingly. But, mere increase in the ionic concentration may not be the only reason for this non-conservative behaviour. For Co, inorganic complexing ligands such as chlorides are weak ligands. Hence other than ionic exchange, changes in biological conditions between fresh and estuarine waters could be invoked. This process could also explain the readsorption effect observed for Co in the postmonsoon season. Pore water infusion of soluble Co may be one of the predominant sources of Co at station 1. Bearing in mind how regularly the surface sediment is disturbed in the estuary and the rate of physical and chemical processes taking place in pore water, it seems unlikely that pore water infusion contribute significantly to dissolved Co in the overlying water column. Since concentration of particulate and sedimentary trace metals were considerably greater than the dissolved concentration observed in this study, desorption from these two phases are highly probable. Furthermore, inverse correlations with nutrient elements (Table C.11) indicate that dissolved Co is not resulted from the remineralization of organic matter even though it is an essential metal.

Thus, the discrepancy in seasonal distribution shown by Co can be attributed to variations in different environmental parameters such as salinity, sediment load, nutrient chemistry, discharge of domestic and industrial effluents and land run-off reaching this area.
Chromium

Chromium is a widespread element in the aquatic systems, though in most freshwaters it is present at only around 1\(\mu g/l\) (Ehrlich, 1996). Cr is found in small quantities in RNA of a few organisms. Cr is one of the less toxic of trace metals, considering its oversupply and essentiality. There are two important oxidation states of chromium in the environment, +3 (as the chromic cation) and +6 (as in chromate and dichromate anions). In well-oxygenated waters, +6 is the thermodynamically stable species. However, +3 being kinetically stable could persist bound to naturally occurring solids. Interconversion of \(Cr^{+3}\) and \(Cr^{+6}\) occurs in conditions similar to natural waters. While oxidation of Cr (III) to Cr (VI) appears to be exclusively abiotic (catalyzed by Mn(IV) oxides), chromate-reducing bacteria appear to be widespread in the environment and Cr(VI) reduction can take place under both aerobic and anaerobic conditions (Wang and Shen, 1995).

In this study, the monsoon period dominated over the other two seasons in chromium content at station 1 and 3. At station 2, premonsoon season showed a peak concentration, whereas, slightly high postmonsoon peak was observed in the estuary. Interestingly, highest annual mean concentration was observed at the estuarine site only for chromium. The order of abundance of the metal was station R > station 2 > station 1 > station 3. Chromium varied from 1.260 to 6.500\(\mu g/l\) at the mangrove stations, from 1.600 to 4.470\(\mu g/l\) at the riverine site and from 1.650 to 14.530\(\mu g/l\) at the estuarine site (table A.36). Seasonal mean variation of dissolved chromium is depicted in Figure 5.6.

![Figure 5.6: Seasonal mean variation of dissolved chromium](image-url)
In the mangrove habitats, processes determining the distribution of chromium are very complex since it is a redox sensitive element. Cr(VI) is easily reduced by Fe( +2) dissolved sulphides and certain organic compounds with sulphydryl groups. The reduced species of chromium has high affinity for particulates and is removed from the system. The reduction of oxygen and increase of hydrogen sulphide favours this reaction. In this study, Cr showed an inverse relation with Fe. This might be due to the increased solubility of Fe under reducing conditions while Cr is adsorbed onto particulates and sediments under this condition. Again, Cr was found to have an inverse relationship with salinity (Table C.2). This may be due to the input of freshwater containing Cr into this site as land run off increases to a considerable extent during the monsoon season. Moore and Ramamoorthy (1992), have shown that municipal waste waters release considerable amounts of Cr into the environment. pH was found to be a factor controlling Cr concentration at station 2 (Table C.2). This could be expected, as Cr is a redox sensitive element. Remineralization of organic matter is found to contribute significantly to the Cr pool of a system (Sirinawin et al., 2000). In this study also, positive correlation between both phosphate and nitrogenous nutrients with Cr was observed (Table C.11) confirming this source.

In the riverine station also land run-off contribute significant amount of soluble Cr. Highest Cr concentration in water was recorded at the time of high freshwater inflow in a study by Mzimela et al. (2003). The heavy influx of freshwater would have promoted desorption of Cr from sediments of the industrialised area to the water column significantly changing its Cr content. Here, Cr was found to co-vary with Zn (Table C.8). This indicates a common source for these two metals. Furthermore, Cr did not show any relation with nutrients (Table C.11) emphasizing an anthropogenic origin.

At the estuarine site, monsoon season recorded a minimum in concentration. This might be due to the dilution of the metal by the heavy freshwater flow. Cr did not exhibit any correlation with the hydrographical parameters and with nutrients (Table C.2, C.11). This non-correlation of Cr with nutrients was observed earlier by Sirinawin et al. (2000). In oxygenated waters, Cr would be present in the thermodynamically stable +6 state. Cr(VI) being more soluble than Cr(III), which
has great affinity for particulates, may explain the elevated Cr concentration observed in the estuary than the river or mangroves.

Nickel

Nickel is an important co-factor in urease, an enzyme responsible for uptake of nitrogen by phytoplankton. It is considered as the weakest reactive element and has least affinity for the particulate phase. Therefore, Ni exists preferentially in the dissolved form (Sokolowski, 2000). Dissolved Ni in unpolluted freshwater usually ranges from 1-3μg/l. Inputs from mixed urban and industrial sources may increase this level considerably.

Dissolved Ni, in this study, was characterized by a premonsoon peak in concentration at all stations. Lowest concentration was observed in the monsoon season at all stations except the estuarine site, where postmonsoon season recorded the minimum (Figure 5.7). At the mangrove sites, Ni varied from 1.857 to 28.85 μg/l, whereas at the riverine site the variation was from 7.194 to 23.46μg/l. the estuarine site recorded Ni in the range 3.486 to 15.79μg/l (Table A.37). ANOVA calculations showed significant variation between seasons, but much less variation in Ni concentration among the aquatic systems (Table B.6). This might be due to the fact that Ni forms inert unknown chelates or macro cyclic complexes that react slowly against scavenging reactions in both oxic and anoxic waters (Magnusson and Westerlund, 1980).

![Figure 5.7: Seasonal mean variation of dissolved nickel](image-url)
Among the mangrove habitats, station 2 showed greater concentration than station 1. Ni pollution results from various sources such as chemical industries, shipyard and cement. The concentration levels were random most probably due to irregular discharge of emanations from the sources and also due to complex water movement in the creeks coupled with diurnal tidal mixing. Bennon et al. (1978) also reported a similar situation in Gulf of Fos, France. Mangrove tannins are found to bind metals rendering them inactive and thereby delaying their bioavailability (Saifulla et al., 2002). The low concentration in water compared to the other two phases is due to precipitation as sulphides in the sediments and complexation with organic matter (Lacerda et al., 1999). According to Moore and Ramamoorthy (1992), Ni forms moderately strong complexes with humic and fulvic acids. If ratios of fulvic acid and Ni are greater than 2, the formation of Ni-fulvic acid complexes is favoured. It is well established that humic substances are found in plenty in mangroves. In a study by Turner et al. (1998), it was revealed that for Ni, scavenging by particles was suppressed by the formation of strong organic complexes.

Highly significant positive correlation with salinity was seen at station 1, while at station 2, the correlation was less significant (Table C.2). The conservative nature of Ni was observed by a number of researchers (Laslett and Balls, 1995; Sanudo-Wilhelmy and Gill, 1999; Hatje et al., 2003; Shiller and Boyle, 1991; Dai et al., 1995). This indicates that variables other than salinity are controlling the levels of metals at station 2. Continuous decomposition of organic matter can also release incorporated metal into the water. Moreover, anthropogenic inputs from the petroleum activities contribute to Ni contamination. Temperature was found to be highly correlated with Ni at station 2 indicating a temperature driven distribution of the metal at this site (Table C.2).

According to Drever (1997), hydrous Fe and Mn oxyhydroxides have high adsorption capacity for Ni, as is evident from their strong correlation between them (Table C.8). Sokolowski (2000) has shown that dissolution of solid Fe could also contribute to the elevated levels of dissolved Ni by release of the metal from Fe oxyhydroxides under anoxic conditions. In this study also, remarkably high correlation between these metals were seen.
Seasonal distribution of dissolved Ni showed a premonsoon maximum and a monsoon minimum at station 3. Desorption from particulate materials and resuspended sediments are possible, as this system experiences a sudden change in ionic strength in the premonsoon period. This change could be expected by the saline water intrusion occurring in this period due to the reduced stream flow. Besides, Ni showed good positive correlation with dissolved Fe (Table C.8) indicating that this metal is associated with the amorphous Fe and Mn oxides, the dissociation of which releases the trace metal adsorbed onto them. Jenne (1968) concluded that fixation of Ni, Co and Zn on soils and sediments is caused by the Fe and Mn oxides present in them.

Herzl et al. (2003) suggested that Ni forms organic Ni complexes with high conditional stability constants and this reaction would limit their dissociation during competition for Ni with suspended particulate matter, and hence their removal. As station 3 is situated near a range of industries, numerous kinds of organic compounds may have leached into the water column. Complexation of Ni with these compounds may account for the elevated levels of soluble Ni. The significant role played by colloids in the transport and transformation of organic matter and associated trace metals such as Cd, Cu and Ni is well established (Dai et al., 1995). Since colloidal particles are abundant in rivers, association with them is yet another important mode of transport. In the Subarnarekha River also, premonsoon season showed maximum concentration (Senapati and Sahu, 1996). Ni could be taken up by or adsorbed onto cyanobacteria (Corder and Reeves, 1994; Asthana et al., 1995; Parker et al., 1998). Diatoms also are capable of taking up nickel hence a mass removal of the metal by these organisms is also possible.

At the estuarine site, dissolved nickel did not vary much between seasons. However, a higher value was observed in the premonsoon, followed by monsoon and postmonsoon seasons. Desorption of Ni from suspended particulates and fine-grained sediments are well recognized (Vazquez et al., 1999; Martino et al., 2002; Elbaz-Poulichet et al., 1999; Ouseph, 1992; Shiller and Boyle, 1991; Dai et al., 1995). Ouseph (1992) has shown that the steady increase of Ni from monsoon to
non-monsoon periods indicates that the longer residence time of finer fraction of suspended solids in the river water facilitating further build-up by ion exchange processes. Ni has shown to have good positive correlation with phosphate at station 3 and R (Table C.11) pointing to the organic regeneration of the metal.

However, none of the hydrographical parameters exhibited any correlation with dissolved Ni at this site (Table C.2). This clearly favours an anthropogenic input of Ni into this estuary. The automotive combustion of Ni-containing diesel oil represents 57% of anthropogenic emissions. About 25% originates from extraction and industrial applications, followed by waste incineration, wood combustion, coal combustion and fertilizer production (Moore and Ramamoorthy, 1992). The Cochin Shipyard located on the banks of this estuary is yet another major source of Ni in this estuary. In the Peconic River estuary, Breuer et al. (1999) observed that 50% of Ni present in the estuary was from anthropogenic source.

**Cadmium**

Cadmium, even in trace quantities, is fatal to biological life. Chemically, it is an oxyphilic and sulfophilic element. Cd is present totally as a divalent species up to pH 8, in the absence of any precipitating anions such as phosphate or sulphide. In this form, Cd²⁺ will be available for sorption onto suspended solids and complexation with organic matter and will be transported in those forms.

Seasonal distribution of dissolved cadmium showed some interesting features (Figure 5.8). Abnormally high values were noted at station 2 and 3 in the postmonsoon period. If these two values are excluded as outliers, station 2 along with station R have premonsoon maximum, with monsoon being the minimum. At station 1, postmonsoon season recorded higher values but monsoon and premonsoon values were more or less same. A monsoon hike in soluble Cd levels was seen at station 3. Cadmium varied from below detectable limit to 6.740μg/l (excluding the outlier), from below detectable limit to 2.670 (excluding the abnormally higher value), and from below detectable limit to 7.740μg/l (Table A.38).
Figure 5.8: Seasonal mean variation of dissolved cadmium

The annual mean concentration recorded the highest at station 2 among the mangroves. The highest concentration in the premonsoon season showed clearly that salinity is an important factor in Cd distribution. Since the chlorocomplexes of Cd is more soluble than the sulphides, Cd has been preferentially desorbed from the particulates and resuspended sediment particles. Furthermore due to the intense anoxic condition existing the mangrove environment, pore water infusion favoured by the degradation of fresh organic matter is likely to occur at this site. According to Gabriel et al. (1987), this pore water diffusion process was very efficient in the Laurentian trough where about 80% of the Cd released was returned to the water column through upward diffusion. At station 1, the lower concentration can be attributed to the intense tidal activity, which wash out the sediments frequently. The oxygenated water at high tide might have a dilution effect. Postmonsoon maximum at this station can be attributed to the greater desorption from particulates. The comparatively quieter conditions during this period would have favoured the longer residence time of particulates in the water column. Again, in the mangroves, pH is found to regulate soluble Cd (Table C.2). Dissolved Cd was found to have well correlated with Zn in the mangroves. This indicates a common source for these metals. Desorption and dissolution from resuspended sediment has been proposed to be responsible for the addition Zn by early researchers (Elbaz-Poulichet et al, 1987; Bayens et al., 1998). As for Zn, in addition to competitive sorption by seawater cations, dissolved Cd is increasingly complexed by chloride ions as salinity increases.
Monsoon season dominated in Cd levels at the riverine site. Moreover, seasonal values were higher at this station than the mangroves. This could be expected from its proximity to industrial effluent discharge points. According to Elbaz-Poulichet (1987), phosphate fertilizers are found to contain large amount of Cd. Since a storage place for fertilizers and insecticides are located on this riverbank, leakages are highly possible. Heavy monsoon rainfall facilitates leaching from soils containing this contaminant and substantial portion of this reaches the river. According to Sholkowitz (1978), a fraction of dissolved Cd in freshwater is present in colloidal state, associated with hydrous Fe oxides and humic acids. This fraction is removed from solution with the colloids at low salinity when flocculation occurs due to the augmentation of the divalent cation activity.

In a speciation study of Cu, Cd and Pb on coastal waters of Kandla-Porbander shelf region, Gorai (1997) found the effects of anthropogenic inputs that mostly occur as complexed forms with inorganic ions and also adsorbed forms. Many other authors have confirmed the anthropogenic source of this metal (Elbaz-Poulichet and Martin 1987; Velasquez et al., 2002). In addition to this, Cd did not show correlation with any hydrographical parameters reflecting its point sources (Table C.2).

In estuaries, cadmium was highly correlated with salinity. Several studies indicated this behaviour for Cd (Boyle et al., 1982; Duinker et al., 1982; Edmond et al., 1985; Salomons and Kerdijk, 1986; Elbaz-Poulichet et al., 1987; Comans and Van Dijk, 1988; Donat et al., 1994; Elbaz-Poulichet et al., 1996; Zwolsman et al., 1997; Kraepiel et al., 1997; Turner et al., 2002; Hatje et al., 2003). High Cd concentration in high salinity season found is attributed to desorption from sedimentary particles. Furthermore, speciation of Cd is dominated by inorganic forms because of competitive adsorption and complexation with seawater ions. The stability and solubility of the chlorocomplexes formed enhance the mobilization of Cd in estuaries and usually prevent the competing readsorption process from occurring (Elbaz-Poulichet, 1987). In addition, the competitive complexation between particulate surface sites and inorganic dissolved ligands depends on the concentration of dissolved ligands and on the complexation constants of these ligands in each environment. It has long been established (Garnier et al., 1996;
Kraepied et al., 1997) that the impact of dissolved inorganic ligands on the dissolved complex formation is ordered as Ag >> Cd >> Zn > Mn, Co > Cs. Competitive complexation with inorganic ligands (mainly Chlorine) may explain why Cd showed the highest desorption rates and why desorption greatly increased with increasing salinity (Comans and van Dijk, 1988).

Hatje et al. (2003) has pointed out that, in low turbidity micro tidal estuary, the contribution of resuspended particles to dissolved Cd maximum is expected to be very limited due to the low concentration of these particles on the mixing zone. Even though Cochin estuary is a micro tidal estuary, the shallow depth of the sampling site promotes resuspension of the sediment to occur by constant wind driven waves and tidal mixing. This activity encourages the release of metals from sediment into the water column. Paul and Pillai (1983) and Ouseph (1992) concluded that solubilization of Cd from resuspended sediments was occurring in this estuary. Moreover, anthropogenic inputs from various industries located near the rivers draining to this estuary are the major contributor of soluble cadmium.

**Lead**

Lead is present in and transported through aquatic systems in both dissolved and particulate forms. The behaviour of lead in natural waters is thus a combination of precipitation equilibrium and complexing with organic or inorganic ligands. The degree of mobility of lead depends upon the physico-chemical state of the complexes formed.

Concentration of lead in uncontaminated freshwaters is generally ≤ 3 μg/l. However, much high level often occur near the high ways and urban regions due to the combustion of gasoline. At the major industrial zones, rivers may contain up to 20-89 μg/l lead (Pande and Das, 1980).

In the present study, lead displayed a distinct monsoon maximum at all stations (Figure 5.9). Except for station R, premonsoon period recorded the minimum. At station R, postmonsoon concentration levels were slightly lower than the premonsoon period. ANOVA calculations showed a significant variation in concentration between months (Table B.6). Highest annual mean concentration was recorded at station 3, the riverine station, while the minimum concentration
was observed at station 2. The mangrove sites recorded Pb in the range 1.460 to 25.96μg/l, while at the riverine and estuarine site Pb varied from 4.62 to 42.76μg/l and 2.42 to 25.01μg/l respectively (Table A.39).

Among the mangroves, station 1 was characterized by high annual mean concentration. This can be expected from its location near the city. Automobile fuels are recognized as the single largest source of lead. Dissolution of lead from the Aeolian fallouts may be the reason for the observed concentration peak. A significant inverse relationship with salinity was observed at this station confirming the atmospheric source of this metal (Table C.2). Many authors have related the absence of dissolved Pb concentration with salinity to the atmospheric input of the metal (Yeats and Campbell, 1983; Balls, 1985; Buat-Menard, 1986). At station 2, lead did not correlate with any of the nutrient elements (Table C.11) suggesting that Pb distribution is mainly controlled by external cycling, such as scavenging, here (Bruland, 1983, Chester, 1990).

The monsoon maximum in Pb concentration can be attributed to the precipitation source of this metal. As Pb is found in large quantity in the atmosphere, monsoon showers would have washed down the atmospheric particulate matter into the aquatic systems subsequently leading to monsoon hike in concentration. The decrease in dissolved lead concentration in the premonsoon season can be attributed to the transfer of dissolved Pb to particulate phase, either by biological uptake or scavenging. Moreover, this tendency is accompanied by a significant correlation with nitrite (Table C.11). Thus the lower values in the
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summer months suggest removal of dissolved Pb to organic particulate matter (by either active uptake or passive sorption) and a partial release of Pb to solution by organic matter remineralization (Schaule and Patterson, 1981, 1983; Brugmann et al., 1985; Lambert et al., 1991; Boyle et al., 1986).

In addition to the atmospheric source, input of Pb from interstitial waters of metal-contaminated sediment is also significant. Martino et al. (2002), has pointed out that this source can function persistently and effectively if there is enough time for benthic anoxia and early diagenesis to be established in the sediments. This is highly possible in the mangroves as the system itself is highly anoxic due to the enormous organic load added to it. Thus, pore water infusion could be another source for this metal.

The riverine station exhibited the highest annual mean concentration in accordance with its location near the industries. The surface water layer is considered as the first reservoir for the discharged materials. The aerosol fallout in the highly industrialized area may lead to high Pb concentration. Due to the high temperature involved in the production processes, the fumes from these factories may contain greater amounts of Pb (Saad et al., 2003). Rainfall acts as an external source by bringing down the particulate matter to the water column. Furthermore, Pb did not exhibit any correlation with the hydrographical parameters confirming its anthropogenic origin (Table C.2). Increased land run-off may be yet another cause for the elevated concentration levels. Due to this abundance of Pb at the polluted site, any natural geochemical behaviour would be entirely masked. A benthic flux of Pb is also possible at this site. According to Tappin et al. (1995), this benthic flux is driven by aerobic decomposition of organic matter at the bottom surface enhanced by the high content of fine-grained fraction with relatively high levels of organic matter (Aller and Beninger, 1981; Irion and Muller, 1990). The lower values in the pre and postmonsoon months may be due to the reduced river flow and the lesser contribution from precipitation (rain).

At the estuarine site also, lead showed a monsoon maximum. This can be related to the heavy rainfall characteristic of this season, which favours in the addition of lead-rich particulates to the water column. This monsoon peak in Pb levels was observed earlier in other studies (Ouseph, 1992, Joseph, 2001) as well.
The comparatively higher concentration observed at this site might have resulted from the polluted rivers draining into this estuary. The observed positive relationship of Pb with the nutrient elements and lower values in the premonsoon period leads to the assumption that a removal mechanism is operating for this metal by the organic particulate matter. Coagulation of the riverine colloids rich in Pb may be taking place at this mixing zone further reducing the dissolved concentration. This precipitation reaction is observed by other researchers also (Cotte-Krief et al., 2002; Riso et al., 1993; Saad et al, 2003; Ouseph, 1992; Windom et al., 1985; Danielsson et al., 1983; Windom et al., 1988; Boyle et al., 1974; Sholkovitz, 1976). Thus the phase of variation observed depending on the sampling stations indicates the complex factors controlling seasonal variations of this metal.

5.3 Particulate Trace Metals

The knowledge of particulate trace metals in less dynamic estuaries can be used to examine and quantify chemical reactivity and pollution sources. The reactivity and dynamics of particulate trace metal in the estuarine region are instrumental to the short-term and long-term fate of metals in shelf seas and the distribution and fluxes of these suspended particles appear to be regulated by the mixing and differentiated settling of a complex assortment of source materials. Particle composition is probably modified, additionally, by biogeochemical reactivity occurring both within the sediment and in the water column during suspended particle transport (Turner et al., 1992; Dauby et al., 1994; Millward et al., 1997). Thus the dominant mechanism that control the concentration of most trace metals in aquatic systems appears to be physical and chemical adsorption on biologically produced particulate matter. Furthermore, Louma (1983 and 1989) had shown that metals present in particulate form are more bioavailable to the aquatic organisms than those in the dissolved phase. In mangroves, trace metals are found mainly associated with particulate matter Lacerda (1998). Thus, for a realistic and complete assessment of river fluxes and potential pollution, the composition of particulate matter is an obligatory parameter in addition to the concentration of the dissolved elements.
Iron, a redox sensitive element, shows contrasting behaviour in aquatic systems depending on the physico-chemical conditions. Fe has an extensive ability to form soluble complexes with naturally occurring organic compounds. But dissolved Fe has a strong tendency to form insoluble hydroxide polymers and due to changes in pH, Eh and ionic strength encountered by river borne dissolved iron in estuaries it may lead to its removal from solution. These amorphous oxyhydroxides of iron act as efficient scavengers for other trace metals. Hence the biogeochemistry of particulate Fe is central to the understanding of trace metal chemistry in aquatic systems.

![Figure 5.10: Seasonal mean variation of particulate iron](image)

In the present study, iron showed highest concentration in all the three phases of occurrence. At all stations, particulate iron showed a characteristic postmonsoon peak (Figure 5.10). ANOVA calculation revealed highly significant variation between months and seasons (Table B.7). The highest annual mean concentration was noted at station 3, as is the case with dissolved phase. Mangrove sites and the estuary exhibited similar concentration levels. Station 2 recorded slightly higher values than station 1. Fe ranged from $0.012 \times 10^3$ to $78.29 \times 10^3 \mu g/g$ in the mangrove habitats and from $0.893 \times 10^3$ to $65.91 \times 10^3 \mu g/g$ at station 3 and from $0.719 \times 10^3$ to $48.76 \times 10^3 \mu g/g$ at the estuarine station (Table A.40).

Iron has an extensive ability to form soluble complexes with naturally occurring organic compounds. In mangrove environments, wide variety of organic
compounds is produced as a result of the remineralization process. A major part of suspended particles, in fact, consists of organic particles (Tanoue et al., 1982). Thus the role of organic materials in suspended particulates is more important than that of the inorganic suspended matter. Further more, Mc Cave (1984) has shown that the suspended particles, which mainly consist of organic material, have a continuous size spectrum. Usually, particles present in aquatic systems are coated with oxide or by various organic entities. It has frequently been suggested that particle coatings may control the metal binding and other surface characteristics of natural sediments (Day et al., 1994). Such coatings may be more homogenous than bulk particles, giving rise to surface characteristics that are relatively independent of particle type (Luther et al., 1998). Thus the presence of organic colloids of humic and fulvic substances in the mangroves might have significantly altered the adsorbing surfaces irrespective of the particle size facilitating increased adsorption of metal on to them.

Benthic animals and rooted plants disturb the simple structure of sediments by burrowing into them or by growing roots. This affect the rate of transport of gases, solute and particulate matter within the sediment and between the sediment and overlying water (Vale and Sundby, 1998). Roots of the plants are efficient conduits of atmospheric oxygen to the sediment and the well-developed aerenchyma system of the roots allows oxygen to diffuse from leaves to the roots. The diffusion takes place in the gas phase and the oxygen not consumed by root respiration is available for diffusion into the sediment. Burrows created by animals have the same function of exchange between the bottom water and burrow water. The diffusion geometry of burrows becomes similar to those of root systems.

The presence of oxygen at the root-sediment and burrow-sediment interface creates local oxidising conditions in otherwise reducing sediments. This affects the chemistry of Fe and Mn, the soluble reduced forms of which diffuse towards these interfaces, where they get precipitated as insoluble Fe and Mn oxides. Thus bioturbation may be the reason for excess particulate iron observed in the mangrove habitats.

Furthermore, many others have opined that the organic matter produced in marshes is seasonally regenerated, producing acidic zone near the surface that acts
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to weather Fe mineral phases (Boulegue et al., 1982; Lord and Church 1983; Ferdelman et al., 1991; Luther et al., 1992; Velde et al., 2003). Iron-rich particle type may be another reason for the enhanced iron levels in particular matter. Removal of Fe (II) by precipitation in anoxic waters was suggested by Gavis and Grant (1986). The relatively large particulate Fe concentration observed in the mangrove waters further strengthens this explanation.

Though ‘colloidal pumping mechanism’ is highly recommended for the settling of Fe in waters, particle coagulation can be operative also. Jannasch et al. (1988) have shown that particle coagulation is more effective in Fe removal from water than colloidal sedimentation. The high concentration of Fe and organic matter in the suspended materials are characteristics of fulvic and humic acid colloids, which are abundant in the mangrove systems. Another important source for particulate Fe in the mangrove habitats is the diagenetic remobilization from the sediments. The role of pore water outflows as a source of Fe and Mn enrichment in suspended matter is also widely recognized (Feely et al., 1986; Sundby et al., 1986; Paulson et al., 1988; Dehairs et al., 1989).

In the present study, particulate Fe showed no correlation with any of the hydrographical parameters except with pH at station 1 (Table C.4). This may be due to the abundance of Fe in the particulate phase and changes in particle composition due to the low chemical reactivity of this metal. Another reason for this non-correlation may be that the distribution of particulate Fe was controlled almost entirely by physical processes (i.e. resuspension and sedimentation). Since particulate concentration is generally high relative to dissolved trace metals, transformations from one to another would not significantly affect the particulate metal levels. Seasonally, postmonsoon was characterized by peak concentration at all the sites. In this period, the relatively calm and quieter conditions in the creek waters might have favoured the longer residence time of particles in the water column and the time available for adsorption of the metal. Ciceri et al. (1992) have shown experimentally that particulate Fe concentration increased over long time scales. In the postmonsoon season, particle concentration was much lower than the monsoon season and consequently a concentrating effect comes into play. Other researchers have related this increase in particulate metal concentration with the
reduction of particle concentration to the accompanied reduction in the buffering capacity of the suspended particle loading (Owens et al., 1997; Turner, 1999).

Particulate Fe showed highest annual mean concentration at station 3, the polluted river site. Fe exists primarily as colloids in freshwater and there is a fair chance for it to form amorphous oxyhydroxides in estuaries. In an experimental study, Wen et al. (1997) found that metals such as Fe and Zn are sequestered from the dissolved phase into particulate phase via colloidal pumping. The rate of colloidal aggregations thus controls the transfer of metal into the particulate phase before its removal from the water column by sedimentation. Though, the colloidal fraction is believed to be pass through 0.45 m filter, Benoit and Rozan (1998) have pointed out that overloading of filters cause a marked decline in the effective pore size of the Fe colloids, eventually leading to complete blockage of Fe from the filtrate fraction. This is a strong possibility in the present study as the fine re-suspended material was in plenty often causing the filter clogging.

However, the most probable source of particulate Fe at this site seemed to be the effluent discharges from the industries and sewage out fall from the urban areas. Ouseph (1992) has opined that rivers draining into the Cochin estuary such as Chitrapuruzha, carry with them increased particulate matter load rich in trace metals from the effluent discharge points. Non-correlation with the hydrographical parameters at this site lends further credence to this explanation (Table C.4).

Monsoon season was characterised by the minimum concentration of particulate iron at this site. This may be due to the dilution effect as a large amount of particles find their way to the river through intense land run-off. Such a decrease in particulate metal levels with increasing particle load was noted elsewhere (Owens et al., 1997; Turner, 1999; Forstner et al., 1989; Zhang and Liu, 2002). The dilution probably occurred as a consequence of the presence of particles having fewer complexation sites. There could also be large mega particles with small specific surface area or they could be composed of materials with intrinsically low abundance of adsorption sites. The postmonsoon hike in particulate Fe concentration may be the result of increased residence time of the particles in the water column facilitating adsorption on to them. The heavy influx
of freshwater in the monsoon season might have increased the sediment resuspension rates. This phenomenon, in turn, promotes injection of pore water species into the water column (Tramontano and Bohlen, 1984). After release into the water column, dissolved Fe gets immediately oxidized and precipitated (Zwolsman, 1994). The oxidative precipitation mechanism may be higher in the postmonsoon period. Moreover, Jarvie et al. (2000) have shown that for the particulate fraction of elements with a strong micro particulate (colloidal) component, such as Fe, the effects of river flow are minor relative to within-river processes.

Hydrous Fe and Mn oxyhydroxides are ubiquitous in the estuarine environment and they have high adsorption capacity for other trace metals. In this study, particulate Fe showed a unique distribution at the estuarine site. Postmonsoon period was recorded with highest concentration similar to the other sites whereas the monsoon season was reported the second highest in concentrations. The annual mean concentration was similar to that of the mangrove sites. In fact, an intermediate value between the two mangroves. At this estuarine site also, hydrographical parameters did not exert any influence on the particulate metal distribution (Table C.4).

The elevated concentration of particulate Fe at this site may be due to the much observed particle concentration effect of salinity. Physical association appears to be important in estuaries in which hydrous oxides are trapped within aggregates of organic matter (Boyle et al., 1977). Chemical association could also be important, in that metal oxides can adsorb some dissolved species (Morris et al., 1981). In addition, metal oxides, organics and metal-organics may form coatings on suspended matter. Fe existing as colloids in the freshwater get precipitated as amorphous oxyhydroxides in estuaries. The removal of Fe by flocculation processes is observed to be up to 70% (Eastman and Church, 1983).

Anthropogenic activities can be a major contributor of particulate Fe in the Cochin estuarine system. Ouseph (1992) has shown that Periyar River, one of the major rivers draining into this estuary brings heavy metals in the form of fine-grained suspended matter from the effluent discharge points. Sankaranarayanan
and Rosamma (1979) attributed the high particulate Fe in the Cochin estuary to the land drainage, harbour activity and sewage.

The postmonsoon hike in concentration may be due to the longer residence time of the finer fraction of suspended solids in river water facilitating further build up by ion exchange processes. The higher concentration during monsoon season than the premonsoon period can be attributed to the increased fresh water run-off, which brings in fine materials to the estuary and the turbulent condition prevailing in the estuary causing sediment resuspension.

Experimental research on metal behaviour up on mixing of river and seawater (Sholkovitz, 1978) has clearly indicated the removal of metals like Fe, from solution to solids. However, experimental studies of the opposite process, release of metal to solution, have given contradictory result (Hoff et al., 1982; Comans and van Dijk, 1988; Gerringa, 1990; Paulson et al., 1991). Thus the influence of salinity on metal adsorption process is not consistent. The low concentration of Fe in the premonsoon season shows that salinity is not the primary factor determining particulate Fe distribution in this estuary. Instead, resuspension of bottom sediments and/or huge amounts of riverine materials may be the deciding factors. Sediment resuspension also promotes injection of pore water species into the water column (Tramontano and Bohlen, 1984). After release into the water column, dissolved Fe is immediately oxidized and precipitated (Zwolsman, 1994). It is clear that diagenetic remobilization can be a major source of Fe and Mn to the suspended matter. Lack of correlation between the hydrographical parameters and particulate Fe (Table C.4) at this site supports the anthropogenic sources and sedimentary inputs of this metal.

Correlation study of particulate Fe with other particulate trace metals showed only a few significant relationships between them (Table C.9). The dissimilarity of Fe and Mn and other trace metals causes difference in their behaviour in aquatic systems. In particular, Fe and Mn are present in suspended particles largely in forms that cannot readily exchange with solution, unlike other metals, which mainly exist as relatively labile surface complexes.
Chapter 5

Manganese

The behavior of manganese in aquatic systems is strongly influenced by its redox chemistry. Although, the oxidation of Mn\(^{2+}\) into precipitatable MnO\(_x\) in aquatic environments theoretically is a slow process, the reaction is catalyzed by pre-existing or freshly generated Mn oxide phases and microbial activity. In fresh waters oxidation exhibits zero-order kinetics with respect to dissolved Mn concentration, the rate is reduced with an increase in ionic strength through occupation of catalytic sites by major seawater cations (Morris et al., 1979; Duinker et al., 1982; Diem et al., 1984; Yeats and Strain, 1990). According to Martin and Maybeck (1979), the average world river suspended matter contains 1050 ppm Mn. Particulate matter appears to be the major mode of transport for Mn as observed in the Amazon, where 90% of Mn was in the particulate fraction (Moore and Ramamoorthy, 1992).

In this study, particulate Mn ranged from 24.13 \(\mu g/g\) to 7023.4 \(\mu g/g\) in the mangrove systems, from 10.69 \(\mu g/g\) to 2966.3 \(\mu g/g\) at the riverine site and from 43.37 \(\mu g/g\) to 2218 \(\mu g/g\) at the estuarine site (Table A.4). Seasonally, postmonsoon was recognized with maximum concentration at all sites (Figure 5.11). Monsoon season recorded the minimum Fe concentration at all sites except the estuarine station. In the estuary, premonsoon and monsoon showed similar concentrations. Mangrove habitats recorded higher concentration than the other systems in almost all seasons. Among the mangroves, station 1 showed higher annual mean concentration while, the riverine as well as the estuarine sites were similar in annual mean particulate Mn content.

![Figure 5.11: Seasonal mean variation of particulate manganese](image-url)
The main pathway of trace metals in the mangrove ecosystems is with the incoming tides associated with suspended particles and Fe and Mn oxyhydroxides (Lacerda, 1998). The intense anoxic conditions inside the mangrove habitats greatly modify the chemistry of the trace elements entering them. The differential solubility of the oxidized and reduced species of Mn greatly influences their distribution in the different phases. The reduced form of this metal is more soluble and in the mangroves, concentration of dissolved Mn detected in this study was very high. However, certain peculiarities of these ecosystems have an upper hand in determining the distribution pattern of different species of Mn. These are the bioturbative and bio-irrigative processes operating in these habitats.

The interactions of plants and animals on intertidal and subtidal sediments greatly improve the exchange of materials between the interiors of the sediments and the overlying water. The roots of the mangrove plants are efficient conduits of atmospheric oxygen to the sediment because of their well-developed aerenchyma systems, which allow oxygen to diffuse from leaves to the roots. The oxygen not consumed by root respiration is available for diffusion into the surrounding sediments. Similarly, many benthic animals construct burrows that are connected to the overlying water. The exchange of burrow water with bottom water allows the transport of oxygen to the interior of the burrows, where it can diffuse into the anoxic sediments. The diffusion geometry of the burrows become similar to those of root systems where large number of burrows permeate the sediment and that in some respects burrows play a functional role similar to that of roots.

The presence of oxygen at the root-sediment and burrow-sediment interfaces creates local oxidizing conditions in otherwise reducing sediments. This affects, in particular, the chemistry of Fe and Mn, whose soluble reduced forms diffuse towards these interfaces, where they are precipitated as insoluble Fe and Mn oxides. This mechanism may account partly for the increased particulate Mn concentration observed in the mangrove environments (Vale and Sundby, 1998).

In the mangroves, influx of Mn enriched pore waters, followed by adsorption onto suspended solids are found to occur (Lacerda, 1999). When dissolved Mn reaches oxidized surface waters enriched in suspended solids, the dominant oxidizing conditions of the flood waters result in the oxidation of Mn(II) to Mn(IV) and
adsorption onto suspended particles. Particulate Mn resulting from the oxidation of the reduced species are also noted by Graton et al. (1990) and Luther et al. (1998). The positive correlation observed between particulate Mn and dissolved oxygen at station 1 (Table C.4) may due to this oxidative precipitation. Regnier and Wollast (1993) have further shown that oxidizing conditions corresponds to higher particulate Mn concentrations. The intense bioturbation in the mangroves might have enhanced the amount of suspended sediments of fine grain size, which facilitated the adsorption of the amorphous oxyhydroxides onto them due to their large surface area. Furthermore, the role of pore water outflow as a source of Fe and Mn enrichment in the suspended matter is widely reported in literature (Feely et al., 1980; Sundby et al., 1986; Paulson et al., 1988; Dehairs et al., 1989).

Elevated concentration of Mn was observed in both the mangrove stations in the postmonsoon period and a minimum in the monsoon. Intense rainfall in the monsoon season may have caused sediment resuspension and increased amount of suspended matter might have had a dilution effect resulting in a concentration levels drop during this season. The relatively calmer conditions of the postmonsoon period would have favoured longer residence time of the particles in the water column. Oxidation of Mn$^{2+}$ to Mn$^{4+}$ is reported to be kinetically a slow process (Moffett, 1994). Furthermore, sorption of Mn has long been recognized as a result of bacterially mediated oxidation (Diem and Stumm, 1984; Moffett and Ho, 1996; Johnson et al., 1995). Since bacterial activity is very high in the mangrove ecosystems, chances for re-adsorption processes can be invoked for Mn during this period. Dissolved Mn concentration was highest in the premonsoon season at both the mangrove sites, while, the particulate fraction was lower. The intense summer conditions would have resulted in greater evapo-transpiration, causing the reduced species to dominate.

At the riverine site, particulate Mn was lower than in the mangrove, just as the dissolved fraction. This can be ascribed to the reduced input of this metal to the river compared to the mangroves. Seasonally, postmonsoon period showed greatest concentration with monsoon season showing the minimum. None of the hydrographical parameters was found to have any influence on the particulate metal distribution (Table C.4) thereby indicating a common source for all these metals. In rivers, Mn is transported mainly in the particulate form (Trefry and
Trace Metals

Presley, 1982). The overwhelming particulate to dissolved ratio for Mn was found to be controlled by the abundant suspended material found in the river. Recent studies have shown that metals like Fe, Mn, and Al occur in the form of colloids (Horowitz et al., 1996; Shiller and Taylor, 1996). Since colloidal fraction of trace metals are found to be in very high proportion in river water, a major portion of Mn may remain associated with them. Furthermore, these colloids are removed with increasing efficiency during the separation process of particulate component as filters get progressively overloaded.

The thermodynamically stable state of Mn in oxygenated waters is +4, which is insoluble. Mn$^{2+}$ is soluble and gets oxidized to Mn$^{4+}$ in an oxidizing environment. The resuspension of fine-grained particles, which may be rich in Mn, from bottom sediments in the comparatively shallow water, may be another source of this metal. In a sorption kinetic study by Ciffroy et al. (2001), it was revealed that re-adsorption on particles was high in the winter season in freshwater. This is possible for metals for which sorption over a long time was found to be predominant. In the case of Mn, oxidative precipitation was found to be kinetically a slow process (Moffett, 1994). Thus, re-adsorption of dissolved Mn species may be another reason for the elevated levels in the postmonsoon season.

Tankere et al. (2000) observed low particulate Mn levels in the surface water in the summer season. He has related this to the inhibition of particulate Mn formation by sunlight. Sunda and Huntsman (1987) demonstrated that sunlight could cause photo inhibition of Mn oxidizing microorganisms. Sunda et al. (1983) also reported on experiments that demonstrated photo reduction of manganese oxides by dissolved organic substances. Such reactions appeared to be important in maintaining Mn in a dissolved reduced form in photic waters. Thus, the increased light intensity in the premonsoon season may be the reason for the observed reduced particulate manganese levels.

Heavy influx of run-off and intense monsoon falls may have acted as diluents in the case of particulate Mn. Turner (1999) and Muller (1994) have shown that both dissolved and particulate metal concentrations are equally sensitive to external metal sources. At this site, the dissolved fraction was highest in the monsoon period while the particulate component was minimum. The
postmonsoon hike thus clearly shows the oxidative precipitation of dissolved Mn onto suspended particles brought in by the heavy land run-off. Besides, Kerala region is well known as a zone of intense weathering. It is quite possible that Fe and Mn leached by the weathering processes were transported through the rivers as finely divided suspended particles. All other trace metals analyzed were found to have strong positive significant relationships with Mn reflecting their common origin (Table C.9). Non-correlation of hydrographical parameters with particulate metal clearly shows an anthropogenic origin of this metal at this site (Table C.4).

The estuarine site also exhibited a postmonsoon hike while the premonsoon and monsoon periods recorded comparable concentration levels. The tremendous volume of suspended material carried by the rivers get flocculated and deposited very quickly upon mixing with seawater. Manganese is a very reactive element and dissolved manganese concentration is low in oxic waters as a result of oxidative scavenging onto suspended particles. Reduced Mn species get oxidized to insoluble Mn oxyhydroxides and amorphous coatings (Giblin et al., 1986; Saager et al., 1997). The freshly formed Mn coatings are very efficient in scavenging additional Mn and Fe as well as other trace metals from the water column. The oxidative precipitation may be one of the sources of particulate Mn in this estuary.

Since rivers draining to Cochin estuary are considered to be polluted, the main contributor of this metal into this estuary may be industrial effluents. According to Ouseph (1992), river Periyar supplies enormous load of suspended matter into this estuary from the various point discharge sources. Particulate Mn, in this study, exhibited no correlation with any of the hydrographical parameters confirming its anthropogenic origin (Table C.4).

In the Scheldt estuary, Netherlands, it was shown that sediment resuspension promotes pore water injection to the overlying water column (Tramontano and Bohlen, 1984). Dredging operations are taking place in the Cochin estuary to maintain the Cochin Harbour. These dredging operations promote sediment resuspension, which further facilitate the release of metals to the water. After release into the water column, dissolved Mn gets oxidized slowly and gets precipitated as particulate oxyhydroxides. Duinker et al. (1980) also observed such a precipitation of particulate Mn by remobilization of the element from the sediments.
Although, desorption of Mn was noted with increasing salinity, readesorption, the amplitude of which depends on salinity, was identified for Mn (Ciffroy, 2001). In addition to ionic exchange, changes in biological conditions between fresh and estuarine water could be invoked for Mn since sorption of Mn has long been recognized as a result of bacterially mediated oxidation (Diem and Stumm, 1984; Moffett and Ho, 1996; Johnson et al., 1995). After the heavy monsoon showers, the disturbed sediments start to settle in the quieter postmonsoon period. The larger, fast settling particles, which mainly include the weakly enriched aggregates quickly redeposit. The finer, slower settling particles stay in suspension much longer. These particles serve as nuclei for the autocatalytic oxidation-precipitation of dissolved Mn, which reaches the water column (Sundby, et al., 1981). Turner (1999) has pointed out that with increasing salinity there is an increasing competition for autocatalytic sites by seawater cations and increasing precipitation of oxidized Mn. This may be the reason for elevated particulate Mn concentration in the postmonsoon season. The concentration levels reported in this study were higher than those reported by Joseph (2001) and lower than those for the neighbouring Kayamkulam estuary (Unnikrishnan, 2000).

Zinc

Zinc shows variable behaviour in binding to particulates depending on the physico-chemical characteristics of the aquatic systems. Zn, as Zn\(^{2+}\), is available for sorption onto suspended mineral colloids and complexation with organic matter. Under natural environmental conditions, the hydroxide formed may even promote mobilization of Zn due to reduction of the cation and increase the solubility of sparingly soluble salts.

In the present study, particulate Zn showed very high concentration in one of the mangroves sites. Rest of the stations exhibited more or less similar values. At station 1, concentration of Zn ranged from 28.19\(\mu\)g/g to 2352.6\(\mu\)g/g, from 16.7\(\mu\)g/g to 1271.4\(\mu\)g/g at station 2, from 16.32\(\mu\)g/g to 1535.95\(\mu\)g/g at station 3 and from 36.12\(\mu\)g/g to 790.6\(\mu\)g/g at station R (Table A.42). Except for the estuarine site, all other stations showed a postmonsoon hike (Figure 5.12). At this station premonsoon exhibited the highest concentration. Minimum concentration was detected in the monsoon period at all stations. Of the metals studied, premonsoon-associated hike in
concentration was observed only for Zn. ANOVA showed a significant variation of particulate Zn both between season and between stations (Table B.7).

![Seasonal mean variation of particulate zinc](image)

**Figure 5.12**: Seasonal mean variation of particulate zinc

Of the two mangrove habitats analyzed, station 1 recorded much higher annual mean concentration than station 2. Station 1 is located near the estuary and is flushed well during the flood period. The concentration levels showed much variation only in the postmonsoon season. This may be due to the point discharge sources present at this site. Mangalavanam (station 1) is located near the urban metropolis where there is high probability for anthropogenic inputs. Storage facility for cement is also located at this site and leaching from this source is another possibility. Petroleum contamination from the huge containers is yet another source of Zn at this site. For the dissolved phase also, this station recorded higher concentration and among the seasons, the postmonsoon period exhibited the peak concentration. Since dissolved as well as particulate concentration were abnormally high at this site, presence of a potential polluting source of Zn presumably from cement and petroleum can be safely inferred.

The intense reducing environment of the mangroves is the primary factor controlling trace metal cycling in these systems. The reducing condition is triggered by degradation of organic matter and consequently, reduced Fe and Mn, and presumably trace metals associated with hydroxide phases are injected into the water column, where they get precipitated or adsorbed on to the suspended matter (Turner and Millward, 2000). Previous studies have emphasized the association of Zn with Fe and Mn oxides (Zwolsman et al., 1997; Windom et al., 1991; Warnken...
et al., 2001). However, these resuspended sediments enriched by Zn by the rapid adsorption of metals released from the reducing pore waters is in a dynamic state of exchange between the water column and bed sediments. In this study also, both the mangrove sites exhibited highly significant correlation between Zn and particulate Fe and Mn reflecting a common source for these metals (Table C.9). At both the stations, particulate Zn did not exhibit any correlation with the hydrographical parameters (Table C.4). This may be due to the anthropogenic sources of this metal. Zwolsman (1997) has further stated that Zn coprecipitated with Mn, and once released from bed sediment re-adsorbs or precipitates as ZnS in the overlying oxygen depleted water column.

Zn is reported to be strongly complexed with organic ligands. The metal may interact in solution with dissolved organic matter by chelation/complexation processes that are, in turn, concentrated by adsorption onto fine particulate such as clay minerals (Piatina and Hering, 2000). Since the finer sediment was found to be a major fraction in the study, the readsorption of Zn is a high probability. Moreover, benthic animals, unlike plants, actually manipulate particles. In addition to simply pushing them aside as they move through the sediments, animals transport particulate matter when they excavate burrows and when they feed (Vale and Sundby, 1994). ZnS formed in the mangroves as a result of sulphate reduction, was found to have get adsorbed or precipitated onto these particles. Van der Sloot et al. (1990) have observed very high particulate Zn in the anoxic zone of Fram Varren Fjord, Norway. He related this to the preferential association of Zn with colloidal mineral phases or with organic fractions.

The possible components of suspended particulate matter in mangroves i.e., Fe and Mn oxides, humic substances and microbial cells are known to have substantially different binding affinities for metals (Ferreira et al., 1997; Green Pedersen et al., 1997). Particle coating may control the metal binding and other characteristics of natural sediments (Day et al., 1994). Such coatings may be more homogenous than bulk particles giving rise to surface characteristics that are relatively independent of particle type. Thus, the great variety of organic coatings present in the mangrove environment would have resulted in a greater adsorption rate.
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Seasonally, the monsoon period showed significantly low values due to the heavy influx of fresh water together with land run off, which might have a dilution effect on the particulate metal present. Introduction of particles depleted in trace metals is highly favoured in this season and results in a reduction in particulate metal concentration. Zn was found to be highest in the postmonsoon period. This hike in concentration may be the outcome of longer residence time of particles in the water column. However, this was also possible in the premonsoon, but Zn is found to desorb to a greater extend as salinity increases (Wells et al., 2000; Hegeman et al., 1992). Thus a hike in postmonsoon may be due to the longer residence time of particle and intermediate salinity both favouring increased adsorption.

Similar to the dissolved fraction, particulate Zn at the riverine site recorded concentration values nearer to that of the estuary. At this site also postmonsoon season was associated with maximum concentration and with a monsoon minimum. Zn showed strong relationship with Fe (Table C.9) indicating an important micro particulate (colloidal) component (Horowitz et al., 1996) for this metal. In rivers, the amount of material transported in the particulate form is much greater than that transported in solution. In heavily contaminated waters, adsorption of Zn onto suspended matter was observed (Martin et al., 1993). As Zn was found to be highly correlated with Fe and Mn, adsorption on to these metal oxyhydroxides is indeed feasible. Fe and Mn oxyhydroxides are found to be amorphous colloids by nature. Laboratory studies conducted on colloids have revealed that trace metals such as Fe and Zn were sequestrated from the dissolved phase into particulate phase via colloidal pumping (Wen et al., 1997).

Postmonsoon hike in concentration observed at this site may due to the increased residence time of slow settling particles facilitating adsorption of metals on to them. In addition to this, mobilization from sediment was enhanced at low river flow conditions (Jarvie et al., 2000). Particulate fraction of Zn showed least values in the monsoon season probably due to the heavy land run off. In this season the dissolved fraction showed the highest concentration showing that major portion of Zn was in the soluble form in the run off water. None of the hydrographical parameters exhibited correlation with particulate Zn (Table C.4) pointing to the
contamination occurring at this site through the effluent discharges from the industries having greater levels of Zn.

In contrast to the rest of the systems studied, the estuary exhibited a premonsoon maximum and a monsoon minimum. In most estuaries studied, Zn was found to be dissolved from particulate matter as salinity increases (Wells et al., 2000; Ciffroy, 2003; Hegeman et al., 1992). However, in this study, Zn showed a positive relationship with salinity (Table C.4). Such behaviour for Zn was reported earlier by Ouseph (1992) in the same estuary and was attributed this increase from monsoon to non-monsoon periods to the longer residence time of riverine particles facilitating further build up of the metals onto them by ion exchange processes. The effluent discharges also affect the usual behavioural pattern of an element. Non-correlation with hydrographical parameters augments this argument.

The elevated levels of Zn may be due to the flocculation processes of Fe and Mn oxyhydroxides as the ionic strength increases. Sediment resuspension may be another possible source for this metal. Fernex (1992) has shown that for Zn, the diffusive benthic flux is of the same order of magnitude as the sorption exchange estimates. Zn, unlike other metals studied, showed negative relationships with other metals (Table C.9). This reflected the anthropogenic source of this metal. The rivers draining into Cochin estuary are considered to be polluted and in addition to this, a zinc smelter factory is situated on the banks of the Periyar River draining to the estuary. Zn is extensively used as a rodenticide and the nearby agricultural areas used for prawn farming might have contributed Zn in this form to the estuary.

**Copper**

In aquatic systems, copper can exist in three broad categories—particulate, colloidal and soluble. Particulates contain varying fractions (12-97%) of the total copper transported by the rivers. Cu interacts strongly with sulphur forming relatively stable insoluble sulphides. Humic materials in natural water bind >90% of total Cu, while those in seawater binds only 10%. In the seawater, Ca and Mg because of their large concentration, displaces Cu from humic acids (Moore and Ramamoorthy, 1992).
In this study, mangrove sites showed much higher particulate copper concentrations than the rest. At all stations postmonsoon season dominated in concentration, while, monsoon recorded the minimum. The order of abundance of particulate Cu at the study sites were station 2 > station 1 > station 3 > station R. The two mangrove habitats did not differ much in copper content. However, in both the monsoon and premonsoon seasons station 1 exhibited comparatively higher values whereas station 2 recorded a distinctly large concentration peak only in the postmonsoon period (Figure 5.13). At the mangrove sites, copper ranged from 7.570 to 653.98μg/g, while at station 3, it varied from 5.03 to 257.84μg/g. the estuarine site recorded Cu in the range 8.220 to 104.07μg/g (Table A. 43).

![Figure 5.13:- Seasonal mean variation of particulate copper](image)

The high concentration of copper in the mangrove systems can be attributed to the well-known ability of Cu to form complexes with organic matter (Kramer and Duinker, 1984; Valenta et al., 1986; van der Berg et al., 1987; Zwolsman et al., 1993). Hirose (1990) has shown that copper was not bound on the suspended particles as inorganic salts but were directly associated with the binding sites of the particulate organic matter. Since organic compounds are abundant in the mangroves, the observed elevated levels may be the result of these stable Cu-organic complexes in particulate matter. Copper in the anoxic Baltic waters showed highest percentage in suspended form (Dyresen and Kremling, 1990). Furthermore, metals like Cu, which are strongly complexed with organic ligands may interact (chelation/complexation) in solution with dissolved organic matter that are in turn, concentrated by adsorption onto fine particulates such as clay minerals (Hirose, 1990). This type of re-adsorption was also observed in an experimental study by Gee and Bruland (2002). They found that Cu is rapidly
removed from the dissolved phase and more than one process was found to control the dissolved and particulate Cu concentration.

Fe and Mn oxides are well known for their ability to act as scavengers of trace metals. Due to the degradation of huge organic matter load in the mangrove environments, Fe and Mn oxides get solubilized under the reducing condition and presumably trace metals associated with hydroxides thereof are injected into the overlying water column, where they get precipitated and/or adsorb onto suspended particles and surficial sediments (Turner and Millward, 2000).

Lead et al. (1999) have shown that Cu binding to particles was relatively insensitive to grain size and compositional variations in suspended particulate matter. Pore water diffusion may be another source of this metal. Furthermore, for Cu, Gee and Bruland (2002) have noted that dynamic exchange of metals between dissolved and particulate phases was of the same order of magnitude or even larger than the benthic fluxes and external sources.

Particulate Cu showed positive relationship with dissolved oxygen at station 1 (Table C.4). This indicates the association of Cu with Fe and Mn oxides, which might have formed in the aerobic environment and the dissolution of which release copper into the overlying water. In addition, Cu showed high correlation with particulate Mn and not with Fe at this site (Table C.9). Fernex et al. (1992) stated that Cu co-precipitated with Mn oxides and not with Fe. Mn also showed positive correlation with dissolved oxygen at this site. Thus, Cu may be present associated with Mn oxides here. At station 2, though, both particulate Fe and Mn correlated with particulate Cu, correlation coefficient with Mn was higher than that with Fe (Table C.9). Hence at this station Cu was associated with both Fe and Mn oxides. The very high concentration of Fe observed at this station also favoured such an association.

The postmonsoon peak in concentration at both the mangrove environments can be attributed to the longer residence time of the particles facilitating further adsorption. Cu is found to desorb from particulates as the salinity increases. This may be the reason for the lower levels in the premonsoon season even though longer residence time of particles in the water column was expected in this season also. Another possibility was the enhanced evapo-transpiration occurring in this
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season leading to intense anoxic conditions. Under these conditions, sulphate reduction is enhanced and Cu may form insoluble CuS, which might have incorporated to the sediments. The heavy influx of monsoon waters may bring with it large ‘mega’ particles impoverished in metal content. The dilution of metal rich particles inside the mangroves with the incoming diluent particles may be the reason for the observed low metal levels in the monsoon period.

The riverine station also exhibited a concentration range similar to that of mangroves. Here also postmonsoon was observed with maximum concentration while, monsoon showed the minimum. In rivers, trace metals are transported in a large proportion as colloids (Hart and Hines, 1994). Of these colloids, the amorphous Fe and Mn oxides and hydroxides are the major fraction and they are found to be good scavengers for other trace metals. In this study, Cu was found to have excellent correlations with both Fe and Mn (Table C.9). This clearly reflects the association of Cu with these polymeric oxyhydroxides.

Cu is used in many industries as catalysts and promoters. The effluents coming from these industries may contain large amount of Cu. The single largest source for Cu in this river may be the anthropogenic inputs. Previous studies have shown that in contaminated rivers re-adsorption of dissolved copper onto particles prevailed (Wangersky, et al., 1989; Gerringa, 1990; Gerringa et al., 1991). In the Vistula River, Sokolowski (2001) observed that Cu existed equally in the dissolved and particulate phases and the influence of suspended particulate matter on its distribution is obvious. Cu showed a negative correlation with pH at this site. Lead et al (1999) have pointed out that removal of Cu from solution in the presence of natural suspended matter is probably the result of rapid uptake of metal onto binding sites at the particle surfaces. This process was found to be pH dependent and can be attributed to competition between the metals and protons for the binding sites (Ferreira et al., 1997; Hamilton-Taylor et al., 1997).

Since Cu exhibited high correlation with Fe, relatively high micro particulate component for this metal is expected. Besides, Benoit et al. (1994) have observed particle concentration effect for Cu. This effect is attributed to the increased colloid concentration in the filtered fraction in proportion to the quantity of suspended matter retained on the filter. Due to the frequent clogging of the filters the colloidal
dimensions of the particles were modified and retained on the filter. This process may partly explain the observed elevated concentrations. Moreover, the dissolved fraction of Cu was found to be lowest at this site clearly showing that majority of the soluble form was colloidal in nature, which might have get retained in the filter due to the particle concentration effect.

Here, Cu exhibited positive relationship only with Ni other than Fe and Mn (Table C.9). This leads to the conclusion that these two metals had a common origin. Seasonally, a monsoon minimum was observed probably due to the dilution by the resuspended particle. Adsorption of Cu on particles would have been favoured in the postmonsoon season due to the longer residence time of the particles in the water column as river flow is reduced. Experimental studies have shown that Cu was found to be increasingly coagulated as the concentration of electrolytes is increased in river water (Sholkovitz and Copland, 1981). This may explain the higher values of Cu in the premonsoon season than the monsoon period.

The estuarine site recorded distinctly low copper content than the other sampling sites under study. Here also, postmonsoon period showed the maximum concentration. Monsoon and premonsoon season showed only a slight variation in concentration. Cu exhibited highly significant correlation with dissolved oxygen and Mn but not with Fe at this site (Table C.4, C.9).

Lower levels of Cu in estuaries were noted elsewhere (Regnier and Wollast, 1993). This can be attributed to desorption and solubilization of riverine particulate matter as the salinity increases. Dissolved Cu in the estuarine waters was found to be largely complexed with organics (Kramer and Duinker, 1984; Valenta et al., 1986; van der Berg et al., 1978; Zwolsman et al., 1993), and desorption from the particulate matter can be expected with increasing pH in accordance with the well known characteristics of humic substances (Bourg, 1983).

Fernex (1992) in a study on the Camargue Delta in France reached the conclusion that Cu co-precipitated with Mn oxides and not with Fe oxides. In the present study also Cu exhibited correlation only with Mn showing that the scavenging particles for Cu in this system were Mn oxides. In addition, Mn showed a positive correlation with dissolved oxygen. The oxidized form of Mn is insoluble
and is formed at a faster rate as dissolved oxygen levels increases. During the precipitation of this oxidized species, it might have sorbed Cu onto it.

The main source of copper to the Cochin estuary may be the effluent discharges from various chemical industries situated on the banks of the rivers draining to this estuary and the intense boat traffic. Cu emissions from the antifouling paint surfaces can be a substantial portion of the copper loading into this estuary. Fishing as well as passenger boats release significant amount of Cu into this estuary. Copper boards and copper nails used in the boats are found to undergo rapid degradation thereby contributing significantly to the copper pool in this estuary. Another possible mechanism is the re-adsorption of dissolved Cu onto particles. The resuspended particles are enriched with the metal by the rapid adsorption of Cu from the reducing pore waters and were in a dynamic state of exchange with the overlying water column (Turner and Millward, 1999). Lead et al. (1999) have shown that Cu binding to particles is relatively insensitive to grain size and compositional variation in suspended particulate matter.

Seasonally, postmonsoon period recorded slightly higher concentration values than the other two seasons. Ouseph (1992) has related this increase from monsoon to non-monsoon months to the increased residence time of riverine particles in this period facilitating further build up of the metal by ion exchange processes. Cu$^{2+}$ was found to have high affinity for humic acids and Sholkovitz and Copland (1981) have shown that metals with strong association with humic acids will also be the ones with greatest extent of cation induced coagulation. Thus the sudden change from the near freshwater conditions of the monsoon season to the increasing ionic concentration of the postmonsoon would have led to an increased particulate metal content.

> Cobalt

Cobalt shows varied behaviour with particulate matter in the aquatic environment (Moore and Ramamoorthy, 1992). About 40-70% of the adsorbed Co was found to desorb from clay minerals. However, desorption from Fe and Mn hydroxides are limited.
In this study, particulate cobalt showed a distinct seasonal distribution pattern in each of the aquatic systems analyzed (Figure 5.14). The highest as well as lowest concentrations were detected in the mangrove systems itself. The order of abundance of Co was, station 1 > station R > station 3 > station 2. The concentration ranged from 0.08μg/g to 26.03μg/g in the mangroves, from 0.04μg/g to 15.5μg/g at the riverine site and from 0.45μg/g to 14.03μg/g at the estuarine site (Table A.44). ANOVA calculations also showed significant variation both between season and stations (Table B.7).

![Figure 5.14: Seasonal mean variation of particulate cobalt](image)

Of the two mangrove systems analyzed, station 1 recorded distinctly high particulate Co content. This station also displayed the highest annual mean concentration while, station 2 showed the minimum. Thus contrasting behaviour was observed in the mangroves. At station 1, Co showed high positive correlation with dissolved oxygen, while at station 2, pH had a positive though much less significant correlation (Table C.4). At both the stations Co showed high correlation with all other trace metals under study (Table C.9). At station 1, monsoon recorded minimum concentration whereas at station 2 premonsoon and monsoon exhibited similar particulate Co levels. At both these sites postmonsoon period was characterised by the maximum metal content.

Co is found to have slightly larger affinity for sorption under anoxic conditions, even though it forms stable compounds under reducing conditions and so will tend to be released to water (Liss, 1976). The observed higher concentration
of Co may be due to increased adsorption on to re-suspended particles. Ciffroy et al. (2003) have shown that with cobalt, inorganic dissolved ligands are weak in complexation reactions and hence re-adsorption mechanism was found to be occurring for Co. The high correlation with Fe and Mn shows that Co is associated with amorphous Fe and Mn oxyhydroxides and removal from these entities was found to be much less. Besides, in mangroves, humic substances were present in enormous quantity and Co$^{2+}$ has least affinity for humic substances (Stumm and Brauner, 1976; Sholkowitz, 1978). Hence Co present in this system will be associated with particles or with amorphous hydrous Fe and Mn oxides.

Sorption behaviour of Co is very sensitive to pH in both fresh and seawater (Liss, 1976). Thus the observed correlation with pH indicates that the change in pH may result in large variation in the concentration levels of Co in the particulates. Furthermore, Benes and Steinnes, (1994), have shown that adsorption of cations to particles increases from almost nil to maximum with increasing pH. The association with Fe and Mn shows why Co co-varies with dissolved oxygen. The oxidized species of Fe and Mn are precipitated while their reduced forms are soluble. Thus with the increase of dissolved oxygen, precipitation of Fe and Mn is enhanced together with Co as these two metal hydroxides are efficient scavengers.

Station 1 was located near the estuary and during high tides the entire forest is covered with floodwaters. The estuary was found to receive huge amounts of effluents from industries. As the metal-rich estuarine water enter the comparatively calm environments of the mangroves, adsorption as well as precipitation occurs leading to high particulate metal content. But, station 2 was of isolated nature. Thus the large amount of particulate Co at station 1 may be anthropogenic in nature. The postmonsoon hike in concentration may be due to the elevated adsorption rate of the metal on suspended particles. Dilution by heavy influx of freshwater containing metal-poor particles may be the reason for the low metal concentration in monsoon.

Station 3, the riverine station showed lower Co concentration than the estuarine site. Here also postmonsoon season was characterized by peak concentration. However, in the monsoon and premonsoon, Co concentration did not vary much, though monsoon showed lower values. None of the hydrographical parameters was found to have any correlation with Co, while all other particulate
metals selected for study showed significant correlation with particulate Co (Table C.4, C.9).

The main contributors of particulate Co to this system are the industrial effluents. Fine-grained particles in the suspended matter may act as nuclei for adsorption to the colloidal Fe and Mn oxyhydroxides, which in turn, adsorb other trace metals onto them. The co-variation of Co with Fe and Mn confirms the association of Co with them. Co may have a strong microparticulate component presumably of anthropogenic nature. Jarvie (2000) has further shown that for metals, which have a high microparticulate component, the effect of river flow, are minor compared to the within-river processes related to tidal conditions, which control mobilization of particulate and microparticulate materials generating huge variations in concentration.

The high colloidal fractions in rivers may have led to the increased particle concentration. Large amount of suspended matter often caused clogging of the 0.45μm filters and there is a fair chance for alteration in the colloidal dimensions of particles. Aggregation of colloidal particles may thus result in elevated Co levels in the filter-retained material. Hydrographical parameters were not correlated with Co. The metal may have been introduced to the river in the form of fine particulates or may have got rapidly precipitated on discharge into the river in the soluble form.

In the estuary, Co presented a different distribution pattern. Here, postmonsoon and monsoon seasons had similar concentrations with a premonsoon minimum. The annual mean concentration was higher at this site than that of the river. Particulate Co showed significant correlation only with Fe and Cr. A significant inverse relationship with salinity was noted at this site.

Zwolsman and Van Eck (1999) noted non-correlation of particulate Co with Mn in the Scheldt estuary. They have related this to the special precipitation dynamics of Mn oxides. Co is preferably present along with sulphides. These metal sulphides are gradually oxidized resulting in release of the metal in the dissolved state whereas Mn gets precipitated upon being oxidized. In this study, salinity was found to be a major factor influencing the distribution of Co. Salinity and Co concentration were inversely related (Table C.4). This type of behaviour was
observed in other estuaries also (Zhang and Liu, 2002). The decrease of metal levels with increasing ionic strength points to the desorption reactions of the metal. The high values shown by the dissolved fraction of the metal in the premonsoon season justifies this assumption. The ion exchange processes as the river water mixes with seawater is the reason for the desorption reactions.

The high annual mean concentration noted at this site points to the anthropogenic inputs to this system. Since Cochin estuary is considered to be contaminated by the effluents from various industries, harbour activities, sewage disposal etc., particulate material was likely to be present at high concentration ranges. In addition, dredging operations are carried out every year to maintain the shipping channel. This resulted in large amount of re-suspended sediments in the water column. Dredging may disturb the otherwise stable sediments, causing them to release metals, which might have got deposited in them. The monsoon run-off might have brought in particles rich in metal content from the industrial discharge points. This may be the reason for the high monsoon value. Adsorption of pore water released metal onto the re-suspended particles was highly favoured in the postmonsoon season resulting in a concentration hike.

**Chromium**

Chromium is a redox sensitive element with an anthropogenic input in many of the aquatic systems. Industrial as well as domestic waste disposals increase the chromium content in natural waters. Cr is one of the less toxic of the trace metals, considering its oversupply and essentiality. The two main oxidation states of Cr in natural water are, +3 and +6. In well-oxygenated water, +6 is the thermodynamically stable species while +3 is the kinetically stable species. Interconversion of $\text{Cr}^{+3}$ and $\text{Cr}^{+6}$ occur in conditions similar to natural waters (Moore and Ramamoorthy, 1992).

Cr, in this study, showed distinct distributional characteristics. The highest as well as the lowest annual mean concentrations were detected in the mangroves. At all stations, postmonsoon recorded the highest concentration (Figure 5.15). In the mangroves, abnormally high values were noted in November. The concentration ranged from 1.35$\mu$g/g to 563.5$\mu$g/g at the
mangrove sites, from 0.300 to 501.47μg/g at station 3 and from 6.550 to 129.52μg/l at the estuarine site (Table A.45).

![Figure 5.15: Seasonal mean variation of particulate chromium](image)

Figure 5.15: Seasonal mean variation of particulate chromium

Of the two mangroves, station 1 recorded higher concentration. The elevated levels of the metal in the mangrove environments can be related to the redox nature of the element. Cr exists as +6 ions in oxygenated waters. But, on entering the reducing condition prevailing in the mangroves, it gets reduced to +3 state rapidly. Moore and Ramamoorthy (1992) have shown that Cr\textsuperscript{6+} is easily reduced by dissolved ferrous sulphides and certain organic compounds with sulphydryl groups. These compounds, are present in plenty in mangroves and hence reduction to Cr\textsuperscript{3+} is highly possible. Aston (1976) has reported that Cr\textsuperscript{3+} is highly sorbed to particulates and suspended sediments. Thus, the high concentration of the metal in mangroves can be due to the reduction of Cr\textsuperscript{6+} ions and subsequent adsorption onto particulate material.

Station 1 was situated near the estuary and was flushed with tidal water regularly. The nearness of the site to the estuary and the domestic sewage discharges into it might have increased the metal content. Municipal wastewaters are found to release considerable amounts of Cr into the environment (Moore and Ramamoorthy, 1992). At station 2 the entry of tidal water is regulated. The isolated nature together with low metal input through anthropogenic sources at this site may be the reasons for the low metal content. Dissolved chromium, on the other hand, was higher at station 2 than at station 1. This points to the fact that at station 2, Cr remained preferentially in the dissolved phase.
At both the mangrove sites, particulate Cr showed very high correlation with the rest of the metals analyzed (Table C.9). This indicates a common source of these metals, presumably the Fe and Mn oxyhydroxides. None of the hydrographical parameters exhibited any correlation with Cr emphasizing its anthropogenic origin (Table C.4). Besides, Cr is likely to be incorporated to sulphidic minerals because Cr$^{3+}$ ($d^3$, $t_{2g}^3$) has high ligand field stabilisation energy (12 Dq) due to its electronic configuration and is kinetically inert to substitution reactions (Burgess, 1988). Thus sulphide will not react easily with Cr$^{3+}$ that is dissolved or supported on solid oxide phases. At both the stations, postmonsoon recorded maximum concentration due to the increased adsorption onto particulates. Lower concentration in the monsoon period may be the result of dilution of the metal-rich particles with incoming metal-impoverished particles of the run-off waters.

Station 3, the riverine station, recorded high particulate Cr content. The main source of this metal in the river may be the run-off from the effluent discharges in the form of fine-grained particles. Various other natural processes such as resuspension, weathering and in situ reduction may have contributed substantially to the Cr pool of this river. In a study by Jarvie (2000) on the River Trent, high particulate component was observed and was attributed to the relatively low tendency of Cr to become associated with particles by scavenging reactions.

Jarvie (2000) has further shown that elements like Cr, with low solubility have greater particulate and microparticulate components. Aston (1976) has stated that Cr has the same concentration both in the oxic and anoxic conditions. Hence, the observed low seasonal variation may be due to the conservative nature of Cr in the oxic and anoxic environment. Since Cr has a strong microparticulate component, colloidal aggregation might have occurred during the separation process of the particulate fraction. Cr exhibited positive relationships with many of the trace metals analyzed indicating a common source of them. Anthropogenic sources of the metal were augmented by its non-correlation with hydrographical parameters. Turner (1999) has reported that sorption reactions are at least partially reversible and there is, therefore, a thermodynamic tendency for particle-water interactions. Adsorption onto re-suspended or previously existing natural particles may be very high during the postmonsoon period subsequently resulting in elevated concentration.
In the estuary, particulate Cr concentration was lower than that in the river and an abnormally high value was observed in December. If this value was excluded as an outlier, monsoon period would have the maximum concentration and premonsoon, the minimum. Estuarine chemistry of Cr is well understood and many studies point to the desorption reaction occurring with increasing salinity (Turner, 1999; Zwolsman and Van Eck, 1993; Salomons and Eysink, 1981). Thus desorption at higher salinity may be the reason for the low metal content in the premonsoon season.

Sedimentary dynamics may be the primary factor determining the particulate metal distribution in the Cochin estuary. As Jarvie (2000) has pointed out, strong linear relationships between Cr and Fe reflected sediment transport processes. Anthropogenic perturbations were highly likely to contribute to a significant fraction of the metal to the estuary. The rivers draining to this estuary were heavily contaminated with effluent discharges from numerous industries. As Ouseph (1992) observed, effluent discharge materials were brought into the estuary in the form of fine-grained particles. Another source of Cr to the estuary is boat traffic. The paints used on the boats contain large quantities of Cr in the form of zinc chromate causing the leaching of which add a substantial amount of the metal to the water. Hydrographical parameters were found to have no significant relationships with particulate Cr, again supporting the anthropogenic source (Table C.4).

Generally, elevated concentration of particulate Cr in the monsoon period indicated that riverine input and run-off from land were the main source of Cr. Since Cr has a large microparticulate component, flocculation is highly favoured as the river water enters the estuary. In a study of suspended Cr from San Francisco Bay, Abu-Sabu and Flegal (1995) noted that processes, which contribute to the enrichment of Cr in suspended matter were weathering and municipal and industrial discharges. Taylor and McClellan (1985) have stated that the weathering process tend to enrich first row of transition elements in suspended particulate matter and sediments.

Nickel

The fate of nickel in the aquatic environment is strongly influenced by its aqueous reactions with soluble species and with particulates. The mechanism by
which Ni can be associated with solid phases is controlled by several important parameters such as pH, pE, ionic strength, types and concentration of numerous organic/inorganic ligands and the presence of solid surfaces for adsorption. Ni binding to particulates in river water exhibits variable behaviour. 97-98% of Ni in the Amazon and Yukon rivers was found to be in the particulate form whereas in some other systems only 5-30% of Ni was associated with particulates (Wilson, 1976).

Nickel, in this study, exhibited a uniform distribution pattern. In the mangrove environment it ranged from 7.63g/g to 135.7µg/g whereas the riverine site recorded Ni in the range 4.1µg/g to 186.4µg/g while at the estuarine site Ni varied from 6.41µg/g to 76.55µg/g (Table A.46). ANOVA calculations showed significant variation between both seasons and stations (Table B.7). Postmonsoon period was characterized by peak concentration at all sites (Figure 5.16). The monsoon season recorded the minimum at the mangrove and riverine sites while similar values were recorded during monsoon and premonsoon seasons in the estuary.

![Figure 5.16: Seasonal mean variation of particulate nickel](image)

The ‘Fisheries’ station (station 2) showed higher annual mean concentration than station 1 (Mangalavanam), which is located near the estuary. The estuarine station (station R) as well as station 1 both exhibited similar annual mean concentration values. Both the mangrove sites exhibited a postmonsoon maximum and a monsoon minimum. Significant variation in concentration between the two mangrove environments was observed only during the postmonsoon period.
Unlike sediments, which can integrate changes in the quality of water column over long periods of time, suspended matter profiles are very sensitive to variations in physico-chemical parameters. In anoxic waters, Ni showed an intermediate affinity for particulate matter (Dyressen and Kremling, 1990). Estimated adsorption rate for Ni is nearly two times higher than for desorption. Increasing particle concentration causes an increase in metal-sorption forward rate constants (Honeyman and Santschi, 1988). In the shallow mangrove waters intense bioturbation may have caused sediment resuspension subsequently resulting in elevated suspended matter concentration. Exchange rate studies between dissolved and particulate forms indicated that sorption processes could result in dynamic internal cycling of Ni, causing concentration fluctuations that can be significant even on daily time scales.

Though Ni complexes strongly with organic ligands (Piatina and Hering, 2000), the metal may interact in solution with dissolved organic matter (chelation/complexation processes) that are in turn concentrated by adsorption onto fine particulates such as clay minerals. Gee and Bruland (2002) have further shown that the exchange of metal between the dissolved and particulate forms are found to be the same order of magnitude or larger than the benthic fluxes and internal sources. Achterberg et al (1997) have shown that Ni-organic complexes are mostly derived from the humic substances and the ligands are mostly aromatic in nature. Since humic acids were found to be present in great concentration in the mangroves, this type of association may be predominant there. In a geochemical study of Ni, Sholkovitz and Copland (1981) have shown that metals like Ni, which most strongly associated with humic acids will also be the ones with greatest extent of cation-initiated coagulation. Thus the higher values at station 2 may be due the presence of huge amount of Ni-humic acid complexes.

Variations found in the mean concentration at the two mangrove stations may be due to the irregular discharges from the polluting sources and also due to the complex water movement in the creek mixed with the semi diurnal tidal mixing. At station 2, particulate Ni displayed significant correlations with other metals suggesting a common origin for these metals (Table C.9). Drever (1997) has shown that Fe and Mn oxyhydroxides have adsorption capacity for trace metals and the adsorption of Ni by such oxyhydroxides was supported by the significant
relationship between Ni and Fe. But at station 1, Ni showed correlation with all metals studied except Fe. This indicates that Ni may be associated with Mn oxides here. Particulate Mn may present, as MnCO₃, while Ni, on the other hand may be partially associated with sulphides. These metal sulphides were gradually oxidized during the restoration of dissolved oxygen with increasing salinity, resulting in release of metal in the dissolved phase. At the same time manganese hydroxides were formed, which are very effective scavengers of trace metals. The close relationship between Ni and Mn indicated that Ni was mobilized from suspended matter but then scavenged back by Mn oxides. The strong positive relationship of Ni with dissolved oxygen also supported this explanation.

Geochemical studies of Ni in rivers showed contradictory results. In the Amazon and Yukon rivers, 97-98% Ni was transported in the particulate form (Moore and Ramaswamy, 1992) while in the Vistula River Sokolowski (1999) found that the dominant transportation mode for Ni was through solution. The strong association of Ni with other trace metals at this study site reflected a common source of these metals presumably the scavenging Fe and Mn oxides. The strong association with particulate Fe pointed to a strong microparticulate (colloidal) component for this metal. Jarvis et al. (2000) have shown that colloids were involved in transferring dissolved Ni to particulate phase. Colloidal pumping hypothesis for transfer of trace metals to particulates is widely recognized (Farely and Morel, 1980; Honeyman and Santschi, 1989; McCave, 1984). It is very important that colloid dynamics were not driven by any change in ionic strength, unlike colloid destabilization in estuaries. Wells et al. (2000) have shown that microbial degradation of colloidal particles released associated metals to solution, whereby metals were transported back to particulate phases via cellular uptake or sorption to particle surfaces.

Investigating the coagulating nature of Ni in river water with various electrolytes, Sholkovitz and Copland (1981) found out that Ni was increasingly coagulated with increasing electrolyte concentration. In pristine river systems, lower reactivity of Ni towards particulate matter was noted. This was attributed to the propensity of the metal to form a range of stable soluble inorganic and organic complexes, which reduces adsorption onto particulate matter (Gerringa, 1990; Bilinski et al., 1991; van der Berg, 1992; Benoit et al., 1994). However, Martin et
al. (1993) in the study on Lena River, Russia, found that the adsorption tendency of the metal increased with the contamination of the river water. Since station 3 was found to receive effluents from a large number of industries, pollution of river water may be very high. Among the major polluting sources of Ni, refineries, shipyard wastes and chemical industries are identified to have an upper hand (Khan, 1995). The highest annual mean concentration was again observed at this site clearly showing the anthropogenic inputs of the metal. The observed increase of particulate Ni from monsoon to non-monsoon periods reflected the enhanced adsorption onto suspended matter in the reduced flow conditions.

Particulate Ni showed some interesting distribution pattern in estuaries. Snodgrass (1980) concluded that Ni concentration in the polluted estuaries were of the same order as in unpolluted estuaries. The concentration and speciation of Ni in estuaries were found to depend on competing processes such as coagulation, precipitation, sorption and complexation/chelation with dissolved organic and inorganic ligands.

At the estuarine site Ni varied linearly with Mn and not with Fe (Table C.9). This can be explained by considering the precipitation dynamics of Mn oxides. The close relationship of Ni with Mn in suspended matter shows that Ni may have mobilized from particulate matter but then scavenged back by Mn oxides. This type of behaviour was observed by Zwolsman and Van Eck (1999) in the Scheldt estuary, the Netherlands. Covariation of Ni with dissolved oxygen can be related to the formation of Mn hydroxides with increasing dissolved oxygen. Mn oxidized to Mn$^{4+}$ and might have carried with it other trace metals by scavenging action.

Adsorption of the metal onto resuspended particles was suggested in previous studies (Honeyman and Santschi, 1998, Gee and Bruland, 2002). Since resuspension was highly possible in the Cochin estuary, readsoption onto fine-grained particles may be an important pathway for the removal of the metal from the water column. However, the coagulative removal of Ni on estuarine mixing was found to be low (Sholkivitz and Copland, 1981). The main contributors of particulate Ni to this estuary were the rivers that carry enormous load of effluents with them. River Periyar, one of the largest rivers draining to this estuary has many chemical industries situated on its banks. The Cochin Shipyard is also located near
the sampling site. Hence emanations from these sources may be the main contributors for Ni in this estuary. Ni can have an atmospheric input as well since automobile fuels contain large amount of this metal.

> Cadmium

A major portion of cadmium is transported to the sea in the solid phase through river suspended matter, rainfall and plain drainage and aerial dust (Martin and Meybeck, 1979; Martin and Whitefield, 1983). A high percentage of total particulate Cd was found in the exchangeable and carbonate fractions of suspended sediments in freshwaters (Moore and Ramamoorthy, 1992). Cadmium sorbed on suspended solids in fresh water may well desorb when river water mixes with saline water.

In this study, Cd showed distinctly high values in the postmonsoon period at all stations. The values were so high in this season that other seasons were almost masked in the graphical representation. The annual mean concentration levels showed a maximum at station 3 and a minimum at the estuarine site. The two mangrove stations showed comparable results. Particulate Cd ranged from 0.95\(\mu\)g/g to 1923.3\(\mu\)g/g at station 1, from 0.68\(\mu\)g/g to 2089.4\(\mu\)g/g, from 1.6\(\mu\)g/g to 3369.7\(\mu\)g/g at station 3 and from 1.6\(\mu\)g/g to 1560.8\(\mu\)g/g at station R (Table A.47). Monthly data showed abnormally high values in January at all stations. Dominant system perturbations occurred in this month might have led to a sudden increase in the Cd content. Seasonal mean variations of dissolved cadmium are depicted in Figure 5.17.

![Figure 5.17: Seasonal mean variation of particulate cadmium](image-url)
Of the two mangrove sites selected for study, station 1 showed high annual mean concentration levels. Seasonally, only during the monsoon season station 2 showed higher values. Due to the intense sulphate reduction in the mangroves, Cd would have got incorporated into the sediments as CdS. The particulate matter concentration in the anoxic waters may be higher than in oxic waters since CdS formed would remain attached to the fine-grained clay particles, which are abundant in these systems. In a study (Dyressen and Kremling, 1990) on anoxic waters, Cd showed a high affinity for the particulate component. Since bioturbation is the major factor modifying sediment nature in mangroves, Cd released in the soluble form by these forces, re-adsorbs rapidly onto the suspended particles. Besides, Cd was found to form stable compounds with organic ligands such as humic substances. Thus the metal could be present in the dissolved fraction also to a considerable extent. However, the sudden increase in concentration in the postmonsoon period may be the result of sedimentation of coarse metal-deficient particles brought in by the monsoon showers leading to the enhanced adsorption onto fine particulates.

At both the mangrove sites, particulate Cd exhibited high correlations with other particulate metals indicating a common source. Anthropogenic inputs are of considerable importance. Hydrographical parameters were found to have no influence on the particulate Cd distribution (Table C.4). This suggested that physical rather than chemical pathways were controlling the cycling of Cd in these systems. Pore water infusion and resuspension can be the major deciding factors for this metal in the mangroves.

Both monsoon and premonsoon seasons recorded much lower concentrations than the postmonsoon period. Desorption of Cd with increase in salinity due to the formation of stable chlorocomplexes have been reported (Comans and van Dijk, 1998; Liu et al., 1990; Che et al., 2003). Complexation of metals with organic or inorganic ligands was found to increase their dissolved component. Hence decrease in particulate Cd in the premonsoon season can be due to the increased desorption associated with increasing ionic strength. Monsoon showers bring with it large 'mega' particles as well as metal-deficient fine particles to the creek waters. Here, they get mixed with resuspended, metal-rich particles causing a reduction in the net
particulate Cd concentration. Piatina and Hering (2000) reported that Cd were associated with finer particles such as clay minerals.

The riverine site exhibited highest annual mean concentration. Here also the postmonsoon period exhibited the maximum concentration. High concentration shown by Cd at the time of low river flow condition points to an anthropogenic input from industrial effluents. Zwolsman and van Eck (1999) observed high particulate Cd levels at low salinity and related this to the anthropogenic inputs. In this study, particulate Cd showed significant correlation with other trace metals. According to Sholkovitz (1976), a fraction of dissolved Cd is present in the colloidal state associated with hydrous Fe oxides. This fraction is removed from solution with colloids at low salinity when flocculation occurs due to the augmentation of the divalent cation activity. Particle concentration effect may be possible for this metal also since it has a strong particulate component (Horowitz et al., 1996).

Adsorption onto particles was found to be highly favoured in the low river flow conditions. The large soluble fraction of Cd brought in by the heavy monsoon run-off might have adsorbed onto suspended solids in the postmonsoon period. Kinetic studies have shown that adsorption of Cd take place at longer time periods (Ciffroy, 2003). Lead et al. (1999) opined that removal of Cd from solution in the presence of natural suspended particulate matter was probably due to the rapid uptake of the metal to the binding sites of the particle surfaces and the pH dependence of this process was attributed to competition between metals and protons for the binding sites. At this site also Cd showed though negative, less significant correlation with pH. The low concentration level in the monsoon season may due to the increases in suspended matter content. Dilution of the solid pool of the metal with suspended matter that has few complexation sites was observed by Noriki and Tsunogai (1992). There could be large 'mega' particles and they may have small specific surface area or they could be composed of materials with intrinsically low abundance of particulate sites.

The estuarine site (station R) recorded the lowest concentration among the aquatic systems studied. As pointed out by Zwolsman et al. (1993), there is overwhelming evidence both from laboratory experiments and field investigations
that Cd bound to suspended matter (partially) was desorbed when river water mixes with seawater (Lead et al., 1999; Shulkin and Bogdanova, 2003; Regnier and Wollast, 1993). The removal is explained as due to the formation of chlorocomplexes. Thus the low concentration levels observed in the Cochin estuary compared to that in the polluted river draining to this estuary is due to the desorption of Cd from riverine particulate matter. Cd was found to be desorbed from particulate matter at the Bang Pakong estuary, Thailand also (Windom et al., 1988). In the Rhine River estuary, Duinker and Nolting (1977, 1978) noticed a 90% removal of dissolved Cd whereas Liu et al. (1990) and Che et al. (2003) observed a re-adsorption of these desorbed Cd onto newly introduced marine particles.

At this site Cd showed high correlation with dissolved oxygen (Table C.4). According to Drever (1997), Fe and Mn oxides are ubiquitous in the estuarine environment. Increasing dissolved oxygen levels favour the formation of insoluble Fe and Mn oxyhydroxides. These amorphous oxides might have scavenged more Cd onto them transforming it to the particulate form. Highly significant correlation between particulate Cd and particulate Mn was observed in this estuary (Table C.9). Lead et al. (1999) found out that Mn oxide fractions showed higher affinity for Cd than Fe oxides.

Postmonsoon season recorded the maximum concentration at this estuarine site. This may be due to the adsorption of Cd onto re-suspended particles facilitated by the increased residence time of particles in the water column. Ion exchange processes might have led to this adsorption. Resuspension of particles was favoured at this site by the dredging of the shipping channel. Ouseph (1992) also observed an increase in particulate metal content in the non-monsoon months. Desorption of Cd from particles with increasing salinity may be the reason for the metal-impoverishment during the premonsoon period. During monsoon, the high energy input due to increased river discharge may cause resuspension of bottom sediments with low metal content accounting for the reduced levels of the element in the particulate matter. Mixing of metal-rich riverine particles with metal-impoverished marine particles may account for the general low level of cadmium in particulate matter in Cochin estuary.
Chapter 5

► Lead

Trace metals are added to the sea mainly via riverine input, weathering, Aeolian transport and remobilization from sediments (Chester 1986; Jickells et al., 1987). Removal is principally controlled by the aquatic cycles of particulate matter through reactions in the water columns and sediments. For metals such as lead that bind strongly to particle surface and have no biological functions, the dominant removal process is by adsorption on to particulate materials, which then sinks and transport the metal to the bottom (Fowler and Knauer, 1986).

Station 3, the polluted riverine site, recorded the maximum concentration in this study and the minimum was observed at the mangrove site (station 2). The order of abundance of lead was station 3 > station 1 > station R > station 2. This order was same as that of the dissolved component. However seasonal distributions of the two fractions presented a different picture (Figure 5.18). Postmonsoon season was dominant in lead content at all stations whereas monsoon dominated in the case of dissolved phase. Pb, which is introduced to the aquatic systems in the soluble form by the monsoon showers, gets precipitated on to particles later, in the postmonsoon period. ANOVA calculations revealed a significant variation between seasons but not between stations (Table B.7).

![Figure 5.18: Seasonal mean variation of particulate lead](image)

Of the two mangrove stations, station 2 showed lower values of particulate Pb than station 1. The concentration ranged from 5.27 µg/g to 392.14µg/g at Mangalavanam (station 1) and from 5.83µg/g to 438.1µg/g at station 2 (Table A.48). At both the stations, correlation with other trace metals was very significant.
pH was found to have an influence on Pb distribution at station 1, while no hydrographical parameters had any influence at station 2 (Table C.4).

Under anaerobic conditions, iron sulphides may be formed through the interaction of Fe with H$_2$S, which is formed by the biological reduction of SO$_4^{2-}$ ions. Co-precipitation of Pb with FeS may occur in the system (Evans, 1989). In addition, iron oxides (and/or hydroxides) may also play a role in the retention of Pb (Forstner et al., 1990; Izquierdo et al., 1997). In this study also, a significant correlation was observed between Fe and Pb. Fernex (1992) has shown that Pb co-precipitated with Mn oxides as well.

Organic matter remineralization was found to release metal to the water column (Regnier and Wollast, 1993). Once released to solution, dissolved lead is removed from the water column by readsorption on to settling inorganic particles, leading to a low dissolved metal concentration. Besides, adsorption on to particles is an irreversible process as evidenced from scavenging models of the metals (Cotte Krief, 2002).

A good positive correlation was found between almost all heavy metals and Pb shows that there were common source or at least one major source for all of them. Hakanson and Jansson (1983) suggested that even metals with quite different chemical properties might appear with similar distribution in nature due to the fact that they are linked to carrier particles with similar properties.

The riverine site exhibited the highest concentration in all the three seasons. The high affinity of Pb to the solid phase is confirmed by experimental (Shulkin and Bogdanova, 1998) and field (Westerlund et al., 1986) studies. Further more, in a study by Jarvie et al. (2000) it was found that Pb showed relatively low tendency to become associated with particles by scavenging and thus had a relatively high particulate component. The anthropogenic input of the metal to the river may be the reason for the elevated metal level at this site. Another mechanism, which affects the particulate Pb concentration, is the readsorption of dissolved Pb, which is released from the sediments on to the suspended particles. Readsorption of Pb in heavily contaminated suspensions was also reported by Regnier and Wollast (1993).
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Colloidal aggregations can be another reason for the observed elevated Pb concentration at this site. According to Zhang and Liu (2002), concentration of Pb in rivers may exceed two fold depending on the water discharge, sediment origin and content and also anthropogenic activities of the drainage basin. Rivers of industrialized areas bring suspended matter enriched with trace metals. Benthic fluxes of particulate Pb was considered as the main source of Pb in the overlying water by Brugmann et al., (1992). The positive relationship of Pb with Fe further points to the sediment transport effects. Significant correlations with other trace metals such as Cu, Zn, Co etc. indicate high similarities in the environmental distribution and chemical behaviour of these metal species.

Estuarine reactivity of Pb is well understood (Shulkin and Bogdanova, 2003; Martin et al., 1993; Regnier and Wollost, 1993). Factors controlling the regional distribution of particulate Pb to the depositional environments are different discharges from petroleum basin, shipping wastes, land–based sources, biological activities and effects of wind. Pb can be released from the antifouling paints and equipments like solders used in ships. The released Pb ions are adsorbed or co-precipitated on to suspended matter found in abundance in the estuary. In the Cochin estuary, shipping activity is high and emanations from these ships constitute one of the major sources for this metal.

In an experimental study on the mobilization of metals from riverine suspended matter on mixing with seawater, Shulkin and Bogdanova (2003) found that Pb remained preferentially in the particulate phase. In the Bang Pakong estuary, Thailand and in the Gota river estuary, Sweden (Danielsson et al., 1983) particulate Pb distribution implied an estuarine removal (Windom et al., 1985).

Pb can have an atmospheric source also (Westerlund et al., 1986; Rojas et al., 1993; Veron et al., 1994; Ferrand et al., 1999). The air-borne particulate Pb contributes either directly to the make up of particulate population, or to a lesser degree, indirectly via dissolution and rapid readsorption on to pre-existing particles. In this study, Pb exhibited preference for particulate Mn as evidenced from its strong correlation with Mn (Table C.9). Fernex (1992) has also shown that Pb co-precipitated with Mn oxides. The observed correlation with dissolved oxygen (Table C.4) also supports this argument. Mn oxide formation is promoted with increasing
dissolved oxygen and these oxides can further scavenge additional metal ions on to them. Thus the main contributors of Pb to this estuarine system are the riverine particles brought in by the rivers flowing through the industrialized areas and the atmospheric input together with contribution from resuspended sediments.

5.4 Sedimentary Trace Metals

The capacity of the sediments to accumulate compounds makes them one of the most important components for the evaluation of contamination levels in aquatic ecosystems. The sediment, after fine particle deposition and adsorption processes, is the main depository of heavy metal accumulation (Silva and Rezende, 2002). Lake sediments can serve as information archive of environmental changes through time (Haworth and Lund, 1984); where each layer of buried sediment would represent a particular record of the past environmental conditions (Von Guten et al., 1997). Elevated metal concentration associated with long-term pollution caused by human activities has been recorded in mangrove sediments (Lacerda et al., 1993; Mackay et al., 1992; Mackay and Hodgkinson, 1995; Tam and Yao, 1998). Mangrove sediment can act as a sink for many heavy metals released to the environment as well as a source of them to the nearby aquatic system (Harbison, 1986). Sediments have thus proved to be excellent indicators of environmental pollution. Thus the determination of trace metals in the sediments becomes an integral part of any hydrogeochemical evaluation of the aquatic environment.

Iron

Iron is a trace metal with very important biological and biochemical functions. Iron oxyhydroxides can act as a major carrier phase for other trace metals in the aquatic environment. Seasonal variations in hydrological flows, in redox conditions, in particle loading, in speciation all significantly influence the distribution of Fe (Davison, 1985).

In this study, Fe in the sedimentary phase exhibited a unique distribution pattern at each site. At station 1, the monsoon period recorded maximum Fe content and minimum concentration was noted during postmonsoon. The other mangrove site, station 2, showed a monsoon maximum and a premonsoon
minimum. The riverine and estuarine sites presented similar seasonal variation with a premonsoon hike and a postmonsoon minimum (Figure 5.19). The order of abundance of sedimentary Fe was station 3 > station 2 > station 1 > station R. ANOVA calculations also showed highly significant variation within the systems (Table B.8).

![Figure 5.19 Seasonal mean variation of sedimentary iron](image)

Among the mangrove habitats analyzed, the ‘Fisheries’ station (station 2) exhibited higher Fe content than station 1 (Mangalavanam). At station 1, Fe ranged from $7.006 \times 10^3$ to $38.58 \times 10^3 \mu g/g$, whereas station 2 showed Fe in the range $15.90 \times 10^3$ to $46.08 \times 10^3 \mu g/g$ (Table A.49). The higher concentration of Fe at station 2 could be related to its environmental setting. Surface sediment sample was collected from the vegetated area at station 1 whereas at station 2, samples were collected from the creek waters. The ability of mangrove plants in modifying the observed geochemistry of many trace metals is well understood (Vale and Sundby, 1994). According to Ross (1994), the fine roots of mangrove plants can affect small changes in soil condition in the rhizosphere, which can influence metal bioavailability and their transfer from soil to plants. Many marsh and mangrove plants have aerenchyma tissues, which can supply oxygen to the roots buried in the anaerobic soils. The amount of oxygen transported to the roots often exceeds the demand of the root tissue, resulting in radial oxygen loss into the rhizosphere (Otte, 1991). Because of this phenomenon, sediments at the vegetated sites have higher redox potential. The reduced state of the bulk sediment might have favoured the mobilization of the metal by the formation of metal sulphides but oxidation processes in the rhizosphere might have immobilized the metal. Cacador (1994)
has reported that metal oxides have been observed to coat the roots of a number of aquatic plant species. The metal oxide plaque on the roots of many marsh plants has the form of thin coatings or stains. In regions where the plants are active most of the year, much thicker FeO coatings around the roots have been reported. These coatings, which have the shape of hollow cylinders, are called rhizoconcretions. Such coatings were seen on the plant roots of the ‘Fisheries’ station (station 2). Thus, presence of such coatings would have significantly affected the sediment Fe concentration at this site.

Seasonally, the monsoon period recorded peak concentration at both the mangrove sites. Heavy influx of runoff water would have brought huge amount of fine sediments rich in trace metals to the creek waters. Non-monsoon periods exhibited lowest concentration at these sites. Resuspension of metal-rich fine sediments may cause an elevation in metal concentration in the water column. The observed increased metal levels in the dissolved and particulate compartments during the same period further augmented this possibility. Another explanation is the intense evapo-transpiration characteristic of the summer periods. Due to this, the reducing condition is intensified in the mangrove sediments and Fe bound to the sediments are released to the water column as Fe\(^{2+}\) ions. Correlation analysis of iron and dissolved oxygen also supports this argument (Table C.3). Fe varied inversely with dissolved oxygen. In contrast to many metals, reduced form of Fe is more soluble in water and, as dissolved oxygen increases, more and more Fe gets precipitated as iron oxides. Fe showed inverse relationship with temperature at station 2, which too can be related to the reducing conditions developed that is intensified with increasing evaporation rates. Hence, hydrodynamic factors can have a decisive role in the distribution of Fe at this site.

Almost all metals exhibited positive correlation with Fe at station 1, while, Cd showed an inverse relationship at station 2 (Table C.10). Thus at station 1, Fe may have acted as the major carrier phase for other metal ion or both of them may have undergone similar geochemical reaction mechanisms. Organic carbon was also found to have significant positive relationship with Fe at both sites. Enrichment of the metal with organic matter in sediments reflects the diagenetic origin of the metal. Vezina and Cornett (1990) have shown that high concentration of Fe and organic matter are characteristic of fulvic and humic acid colloids, which
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are very abundant in the mangroves. Humic and fulvic acids are reported to have high Fe content (Hung et al., 2000).

At station 1, Fe correlated well with Zn, Cu, Co and Pb and less significantly with Cr, Ni and Mn. However, Cr and Ni were found to be highly correlated to Mn (Table C.10). Thus, except for these two metals, Fe oxides appeared to be acted as the adsorbents. Although laboratory studies showed hydrous Fe oxides to be excellent adsorbers of other trace metals, at station 2, no such correlation was observed except for Cd, which showed an inverse relationship with Fe (Table C.10). This indicates the purely anthropogenic origin of Cd. In a study by Velde et al. (2003) in the French salt marshes, Fe correlated well with Ni, Co, Cr while, poor correlation was observed with Co and Mn.

Among the trace metals, Fe was the most abundant metal in this study and the Fe concentration observed in this study were similar to those reported by Rini (2002). Several studies (Harbison, 1986; Lacerda et al., 1993; Tam and Wong, 1993, 1995; Ong Che, 1999) have shown that mangrove sediments have a high capacity to retain heavy metal from tidal water and storm water run-off, and therefore often act as sinks for heavy metals. Church and Scudlark (1998) have pointed out that trace metals are trapped as oxides at the surface and as sulphides below with limited release in the marsh sediments. Redox sensitive elements like Fe precipitate above as ferric hydrates and are recombined below as mono or pyretic sulphides. Furthermore, elevated metal concentration related to long-term pollution caused by human activities has been recorded in mangrove sediments (Lacerda et al., 1993; Mackay et al., 1992; Mackay and Hodgkinson, 1995; Tam and Yao, 1998).

The riverine station (Chitrapuzha) recorded highest annual mean iron concentration than other systems in this study. Premonsoon season recorded maximum concentration here, while minimum was observed during the postmonsoon period. The overall high metal content and the premonsoon maximum characteristic of the station point to the severe contamination of the river. During the dry season, the river sediments absorb trace metals and organic pollutants discharged freely from domestic and industrial sources without much treatment. Since many industries are located on the banks of this river,
contamination from effluents discharged from these industries may significantly contribute to the Fe pool of the river. In a previous metal speciation study, Joseph (2001) noted a premonsoon maximum in a nearby site. In the highly polluted Subarnarekha River, east coast of India, premonsoon hike in sedimentary iron was reported (Senapathy and Sahu, 1996).

Immediately after the monsoon, trace metals in the river sediments are released to the overlying water and then discharged to the estuarine and coastal environments resulting in a reduction of the metal levels in the sediments during the postmonsoon season. Abnormally high metal concentration in the particulate matter collected during the same period further reflects the resuspension process occurring during the period. Enrichment of Fe in suspended sediments was also reported in other Indian rivers. In the Godavary River, Fe was enriched by a factor of 2-3 times than the bed sediments (Biksham et al., 1991), whereas in the Krishna River, suspended sediments contained as much as 25 times more Fe than the sediments (Ramesh et al., 1990). The suspended solids are finer in nature and are richer in multiple hydroxide coatings, organics and trace metal scavenging clays (Forstner and Wittman, 1981). In addition, hydrodynamic conditions, which influence the movement of bed and suspended sediments are different. Hence particulates in most rivers show heavy metal enrichment relative to bed sediments. Subramaniam, et al. (1987) reported that suspended solids were 5-10 times richer than the bed sediments in the Ganges and Brahmaputra rivers.

Fe did not exhibit any correlation with hydrographical parameters (Table C.3). This fact again emphasizes the anthropogenic source of Fe in this riverine system. Here, Fe showed significant positive correlation only with Ni, though Cu exhibited a less significant correlation (Table C.10). This indicates a common fate of these metals in this river sediment. Total organic carbon was also found to be highly correlated to Fe (Table C.12), pointing to the complexation of the metal in the sedimentary environment presumably with humic substances. Diagenetic enrichment of Fe in the surface sediments is well documented (Zwolsman et al., 1993; Valette-Silver, 1993; Brecker, 1993; Spencer, 2002). In the upstream stations of a Taiwan River, Fe content in humic and fulvic acids were high compared with the coastal locations (Hung, et al., 2000). Another reason for the extremely high Fe content may be the nature of sediment in this study area. Silt and clay mineral
particles are well known for adsorption of the metal cations onto them due to the increased specific surface area. The concentration range observed in this study was in accordance with those reported by Joseph (2001) in the same river.

The estuarine site recorded much lower sedimentary Fe than the riverine and mangrove habitats in this study. Here, iron ranged from $5.427 \times 10^3$ to $15.29 \times 10^3$ µg/g. Seasonally, premonsoon period recorded highest concentration, while, monsoon and postmonsoon exhibited similar concentration. The distinct low content of Fe in the estuarine sediments can be related to the sand dominance of the substratum. Due to the intense tidal action, dilution of the metal-rich fluvial sediments with the metal-impoverished marine sediments would have occurred, which was reflected in the lower metal content.

However, Fe at this site too was present in much large amount compared to the other elements. Diagenetic enhancement of Fe and Mn in the surface sediments of the estuaries is well documented (Zwolsman et al., 1993; Valette-Silver, 1993; Brecker, 1993; Spencer, 2002). With burial, microbial degradation of organic matter take place resulting in bacterial utilisation of oxygen and other inorganic oxidizing agents (Santschi, et al., 1990; Buckley, et al., 1995). The reduction of Fe$^{3+}$ species results in the mobilization of the metal and diffusion to oxic surface sediments where they get precipitated either as oxides or occasionally as carbonates (Farmer and Lovell, 1984). Enhancement of Fe oxides at surface sediments occurs at lower depths than Mn (Cochran et al., 1998). Fe showed significant positive correlation with organic matter (Table C.12) in this study, supporting its possible diagenetic pathway.

In the Beypore estuary, Kerala, Fe was predominant in the clay mineral lattices, Fe bearing heavy minerals and also in the adsorbed state on the surfaces of other minerals and total organic carbon (Nair and Ramachandran, 2002). Positive loading of total organic carbon and Fe$_2$O$_3$ in this estuarine sediment was a reflection of difference in their chemical partitioning pattern. Silt, clay and total organic carbon control the distribution of Fe in this study. Another possible source of Fe is the industrial effluents discharged to the rivers draining into this estuary. During the high-energy periods of the monsoon, increased amount of polluted material might have reached the estuary.
Seasonally, premonsoon season recorded maximum Fe content. In accordance with the sediment enrichment, both the dissolved and particulate components were low, during the same period. Since residence time of particles was found to be high during the summer periods, adsorption and subsequent flocculation of particles would have favoured. The coagulated particles might have settled to the bottom. Furthermore, immediately after the heavy monsoon rain, sediments are highly disturbed and resuspension of metal-rich finer fraction was possible. The depletion of metals from sediments during the postmonsoon period and subsequent enrichment in the particulate and dissolved segments point to the fact that resuspension of sediment was occurring in the estuary during this period.

In a geochemical study of Fe in the Vembanad Lake, of which Cochin estuary forms a part, Padmalal and Seralathan (1991) found that as soon as the reducing condition is developed in the sediment column, Fe\(^{2+}\) in the oxidized zone of overlying waters might get precipitated as ferric complexes. Fe showed strong relationship with organic carbon suggesting that the major source of the element is the organic matter decay.

Fe showed, though less significant, a positive correlation with salinity at this site (Table C.3). This can be due to flocculation and precipitation of colloidal particles to the bed sediment as salinity increases. Of the metals studied, Fe exhibited high positive correlation with Cu, Zn and Ni, while Cd was correlated with Mn (Table C.10). This indicates that for Cu, Zn and Ni, hydrous Fe oxides are the major adsorbing phases. Such correlations were seen in sediments of Laucula bay, Fiji, also (Morrison et al., 2001). The sedimentary Fe concentration in the present study was much lower than those reported by Joseph (2001) in the Cochin bar mouth region, while in line with those observed in Kayamkulam estuary (Unnikrishnan, 2000).

**Manganese**

The chemistry of manganese in aquatic sediments is highly influenced by the physico-chemical status of the system. Manganese is found to be relatively mobile in the aquatic environment. In this study, Mn showed large variation in concentration in the diverse systems analyzed. In the mangrove environments, Mn ranged from 66 to 444.3µg/g, from 47.08 to 627.4µg/g at the riverine site and the
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Estuarine site recorded Mn in the range 34.19 to 171.9 µg/g (Table A.50). ANOVA calculations also showed highly significant variation between stations (Table B.8). Highest annual mean concentration was recorded at station 3, Chitrapuzha River, while the lowest was recorded at the estuarine site. Both the mangrove habitats exhibited similar concentration levels.

Seasonal mean variation of dissolved manganese is depicted in Figure 5.20. In the mangrove environments, postmonsoon season recorded the lowest concentration. Though monsoon period recorded slightly higher Mn level at station 2 than the premonsoon period, both the seasons were found to have similar Mn content at station 1. Premonsoon hike in concentration was also seen for the dissolved fraction also whereas, the particulate metal at both the sites showed highest concentration during the postmonsoon period. Sediment resuspension, which results in reduction of the metal content of the sediments, may be taking place in the postmonsoon season. It may be noted that it was only during the monsoon season sedimentary Mn exceeded the particulate metal concentration at both the sites. Enormous load of sediments brought in by the increased land run off during the monsoon season might have explained this. Thus, during this season, the influx of runoff water, which is rich in fine-grained sediments may have resulted in elevated metal concentration.

![Seasonal mean variation of sedimentary manganese](image)

**Figure 5.20:** Seasonal mean variation of sedimentary manganese

The enhanced levels of Mn in mangrove sediments compared to the estuary can be related to the environmental setting of the two systems. The muddy nature
of the mangrove substratum can hold great quantities of metals onto them, and as Church and Scudlark (1998) have pointed out, metals were trapped as oxides at the surfaces and as sulphides below with limited sedimentary release in the marshes. However, more easily reduced element like Mn can be released to the tidal environment for export to the nearby estuary. Mn oxidation is accelerated by the presence of Fe oxides in the sediments. Since Fe was found to be present in huge quantity in these mangroves, precipitation of Mn as oxides is highly favoured.

The observed enrichment of Mn in the suspended particulate matter can be related to the reducing condition existing in the mangrove habitats. Unlike many metals, reduced species of Fe and Mn are more soluble than their corresponding oxides. Hence, under the anoxic condition, Mn$^{2+}$ ions may form in the sediment pore waters and may have diffused into the overlying water column. This could ultimately result in a reduction of the metal in the sediments. However, rooted plants and burrowing animals can affect the accumulation rate of trace metals as well as their distribution within the sediment (Vale and Sundby, 1994). In the intertidal regions, presence of plants slows down the currents and favours the settling of fine-grained particulate matter. This increases the accretion rate as well as the trace metal accumulation rate because of the higher specific surface area of the fine-grained materials. Like wise, much of the accreting matter consists of high content of plant debris enriched in metals.

In addition to this, presence of oxygen at the root-sediment and burrow-sediment interfaces creates local oxidizing condition in otherwise reducing sediments. This affects in particular, the chemistry of Fe and Mn, the soluble reduced forms of which diffuse back to the interface, where they get precipitated as insoluble Fe and Mn oxides. Mn accumulates at the burrow interface as a result of intense decomposition processes in the burrow lining and mobilization of the metal from the adjacent sediments.

Mn showed high degree of positive correlation only with pH at station 1 (Table C.3). Here, dissolved oxygen was, though less significantly, inversely correlated with Mn. In the sediments, due to the intense reducing condition, pH is lower and Mn may have migrated to the overlying water column as Mn$^{2+}$. But at the surface, due to the presence of oxygen, pH is increased and the reduced species
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precipitated as Mn oxides. Mn was correlated well with organic matter at this station (Table C.12). However, at station 2, no such correlation was observed, yet, the clay fraction showed enrichment of the metal (Table C.3).

At station 1, Mn exhibited significant correlation with metals such as Co, Cr, and Ni (Table C.10) indicating that major adsorbing surfaces for these metals were the Mn oxyhydroxides. For the rest of the metals studied, Fe may have acted as the major carrier phase. Little affinity for organic matter was observed for Mn at this site. Cauwet (1987) observed no enrichment of Mn in the finer fraction of the sediment. However, at station 2, no such relations were noted. Thus at this site, Mn would have experienced different geochemical pathways than at station 1.

The riverine site exhibited highest annual mean concentration among all the sites. Seasonally, the monsoon period was associated with a concentration hike, while, the other two seasons exhibited lower, but similar concentration levels. Only during the monsoon season, sedimentary Mn concentrations were higher than the corresponding particulate metal concentration. Dissolved metal also was highest during this season. All these clearly point to the fact that the major source of Mn in this system is the heavy terrestrial runoff during the monsoon period. Since many industries are located on the banks of this river, effluents discharged from them may be the single largest source of this metal. Moreover, Mn did not exhibit any correlation with hydrographical parameters at this site. In a previous study by Joseph (2001) also a monsoon hike in Mn concentration was observed.

During the non-monsoon periods, suspended particulate matter showed greater Mn content than the sediments. Ramesh et al. (1990) also observed such enrichment in the suspended solids of the Krishna River, India. The suspended solids are finer and are richer in multiple hydroxide coatings (Forstner and Wittman, 1981), organics and trace metal scavenging clays. Thus particulates of most rivers may show metal enrichment relative to the sediment. Studies done on other Indian rivers confirmed the particulate matter enrichment of the metal (Biksham et al., 1991, Subramianiam. et al., 1987).

In this study, Mn showed high correlation with sedimentary organic carbon. Scholkovitz (1976) reported significant metal association with organic matter. This fact is further exemplified by Hunt (1981), who suggested that trace metal
enrichment was dictated by total organic carbon content in sediments possibly through exchange reactions. Organic flocculent coatings also greatly affect the adsorption capacities for trace metals of sediments. A high degree of positive correlation observed between sedimentary organic carbon and the metal, is a testimony to this. Hung et al. (2000) have pointed out that humic substances present in river sediments have a high complexing capacity with Mn.

Metals like Zn, Cd and Pb correlated well with Mn at the riverine site (Table C.10). The affinity shown by these metals towards Mn clearly reflects the coprecipitation of these metals with Mn oxyhydroxides in the river environment. In a study by Morrison et al. (2001), Mn was found to be correlated with Fe, Zn and Cu and inversely with Pb. However, in this study, no correlation with Fe was observed. According to Ambatsian et al. (1997), important transformations are occurring for Mn in the surficial sediments than for Fe since Mn is easily reduced than Fe and a great part of Mn is dissolved in the first stage of diagenesis.

At the estuarine site also, postmonsoon season recorded the lowest concentration. This site showed much lower annual mean Mn concentration than the other three sites. Here, the range of sedimentary Mn was from 34.19 to 169μg/g. Premonsoon season recorded slightly higher values than the monsoon period. Since the particulate fraction was observed with maximum concentration in the postmonsoon season, resuspension of sediments might have occurred during this period resulting in a subsequent reduction in sediment metal concentration.

The major contributors of Mn to this estuary may be the rivers draining into it. Since sedimentation rates are faster in estuaries, metal-rich riverine suspended matter gets incorporated to the estuarine sediments. In addition to this, diagenetic enhancement of Mn in the surface sediments of estuaries is suggested (Zwolsman, et al., 1993; Valette-Silver, 1993; Bricker, 1993; Spencer, 2002). With burial, microbial decomposition of organic material takes place resulting in bacterial utilization of oxygen and other inorganic oxidizing agents (Santschi et al., 1990; Buckley et al., 1995). The reduction of Mn⁴⁺ species results in the mobilization of this metal and diffusion to oxic surface sediments where they get re-precipitated as oxides or occasionally as carbonates (Farmer and Lovell, 1984). As Finney and
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Huy (1989) have pointed out, diagenetic recycling may contribute to enhancement of trace metal concentration in the upper surface sediments.

Because of the thinness of the oxidized layer, some of the upward diffusing Mn escapes to the water column. Particulate Mn is also removed from the surface sediments by periodic resuspension. The larger, fast settling particles, which mainly include the weakly enriched aggregates quickly re-deposit. The finer, slower settling particles stay in suspension and serve as nuclei for the auto-catalytic oxidation-precipitation of the dissolved Mn, which reaches the water column (Sundby and Silverberg, 1981). Chester et al. (1988) described this process as ‘Mn trap’. Studies done on estuaries elsewhere also pointed to similar conclusion (Chen et al., 2000; Chester et al., 1990).

Among the hydrographical parameters, only dissolved oxygen exhibited any correlation with Mn (Table C.3). Here, dissolved oxygen varied inversely with sedimentary Mn. This clearly indicates the diagenetic enrichment of the metal in the sediments. Sedimentary organic carbon also displayed significant correlation with Mn (Table C.12). It has been reported that many metals are strongly complexed by organic ligands. Thus, metals may interact in solution with dissolved organic matter by the chelation or complexation processes and are, in turn, concentrated by adsorption onto fine particulates such as clay minerals (Piatina and Hering, 2000). In this study also, significant correlation with the clay fraction of the sediment was observed (Table C.3). Hence the process undergone by Mn in this estuary may be the oxidative precipitation and subsequent incorporation into the finer sediments.

The sediments were mainly sandy in nature at the estuarine sampling site. Furthermore, due to the high tidal activity, considerable dilution of the fluvial sediments with the marine sediments may also have taken place. Thus the dominance of sand, which is a poor-adsorber of trace metals and the dilution of the marine sediments might account for the general reduction in the metal content observed in this estuary.
Zinc

Zinc is considered as a biologically essential element. It plays a vital role in the biosynthesis of nucleic acids, RNA and DNA polymerases. In the aquatic environment, Zn is enriched in the sediments. According to Moore and Ramamoorthy (1992), total Zn in freshwater sediments of uncontaminated areas is <50μg/g. A similar range was reported for estuarine and coastal areas. However, in the vicinity of industries, Zn concentration often exceeded 100μg/g.

![Graph showing seasonal mean variation of sedimentary zinc](image)

Figure 5.21:- Seasonal mean variation of sedimentary zinc

After Fe, Zn is the most abundant element in this study. This metal showed remarkably high concentration in the mangrove environment. The order of abundance of the metal in this study was, station 1 >> station 3 > station 2 > station R. At station 1, the concentration was as high as 362.98 μg/g. Monthly data showed Zn in the range 46.67 to 362.98 μg/g here (Table A.51). Seasonally also, Zn showed higher content in sediments than the other mangrove site (station 2) analyzed. Seasonal mean variation of dissolved zinc is depicted in Figure 5.21. Dissolved as well as the particulate concentration of this metal was quite high at this station indicating a point source of this metal. Contamination from petroleum storage tanks and cement storage facility located near the sampling site, may partly explain the elevated concentration of the metal in the sediments. Furthermore, sediments were collected from the vegetated area at station 1 and due to plant respiration and animal burrowing, local oxidizing microenvironments may be created in the sediment. Vale and Sundby (1994) have shown that Zn accumulates
at the burrow interfaces as a result of intense decomposition processes occurring in the burrow linings and the mobilization of the metal from adjacent sediments.

Microbial degradation of the huge amount of organic matter in mangrove mud generally removes all oxygen from sediments below the surface layer, creating ideal condition for bacterial sulphate reduction (Berner, 1983). When photosynthetic oxygen production ceases in the night, hydrogen sulphide diffuses through the mud and escapes to the shallow water covering sediments (Hansen et al., 1978). Metals dissolved in this water as free ions or metal-humate complexes are then deposited as sulphides (Pauli, 1975). Thus, incorporation into the sediments as metal sulphides may be another pathway for Zn in the anoxic environments. Moreover, many authors have opined that elevated metal concentration related with long-term pollution caused by human activities is recorded in mangrove sediments (Lacerda et al., 1993; Mackay et al., 1992; Mackay and Hedgkinson, 1995; Tam and Yao, 1998). Similarly, several studies (Harbison, 1986; Lacerda et al., 1993; Tam and Wong, 1993, 1995) have shown that mangrove sediments have a high capacity to retain heavy metals from tidal water and therefore they often act as sink for heavy metals. The estuarine water flooding the mangrove sites was contaminated with Zn from the industrial effluents and hence adsorption of the metal from the tidal waters may also have contributed to the sediment metal concentration at station 1.

Seasonally, monsoon recorded peak concentration at station 1 and minimum was observed during postmonsoon period. However, at station 2, no significant seasonal variation was able to observe. At station 1, Zn exhibited higher concentration in all the three phases such as dissolved, particulate and sedimentary. This clearly indicates that leaching from ‘Zn rich pockets’ may be the reason for the elevated metal content at this site. At station 2, dissolved concentration was found to decrease as sedimentary metal increased. This may be due to the strong soluble complexes that Zn forms with reduced sulphur (Emerson et al., 1983), which will increase the migration of Zn to the water column (Huerta-Díaz and Morse, 1992).

Dissolved oxygen was found to correlate inversely with Zn at station 1 (Table C.3). This may due to the increased precipitation of Zn as ZnS as dissolved
oxygen diminishes. Salinity correlated negatively with Zn at station 2 and may be
due to the dilution of the metal-rich sediment by the large quantity of incoming
metal-deficient sediments in the monsoon runoff. Considering the relationship of
Zn with other metals, highly significant correlations were seen between Zn and Fe,
Cu, Co, Ni and Pb at station 1. Fe correlated positively, yet less significantly, at
station 2. Ni showed positive correlation with Zn at this site also (Table C.10).
These correlations point to the common geochemical processes undergone by these
metals in the mangrove sediments. At both the mangrove habitats, Zn was enriched
in the finer sediments to a considerable extent in this study (Table C.3). This may
be due to the large surface area of the fine particles and due to the surface
properties of clay minerals. Thus enrichment on fine particles shows the control of
size over Zn concentration.

Zn concentration recorded in previous studies showed wide variations. In the
study by Rini (2002), Zn varied from 43.56 to 940.46μg/g in the Vypeen
mangroves; while, Badarudeen (1997) reported Zn in the range 15 to 91 ppm in the
same area. In the Cauvery mangroves, Seralathan (1897) observed Zn to vary
between 76-107ppm. However, studies done elsewhere showed much higher Zn
concentration. In the mangrove sediments of southeast Gulf of California, Zn
ranged between 46.4 to 347.8 mg/kg (Soto-Jimenez and Paez-Ozuna, 2001);
whereas, Ong Che (1999) observed much higher Zn concentration in the Mai Po
mangroves, Hong Kong. Here Zn varied between 148 to 513μg/g.

At the riverine site, Zn varied from 19.59 to 156.8μg/g with the peak
concentration in the monsoon season. Non-monsoon seasons did not show much
variation in concentration levels. The main source of Zn into this river may be the
effluents discharged from various industries. Metal enrichment in the sediments
can be related to the removal of the metal from solution by terrestrial organic
matter, which eventually becomes incorporated to the sediment. Maximum
concentration of the metal during the monsoon period may be the result of heavy
influx of metal-rich particles associated with the runoff water. The increased
amount of particulate matter along with suspended sediment load brought into the
river may have settled at a faster rate enhancing the sediment metal concentration.
Lower concentration during the summer period may be the result meagre terrestrial
runoff. Positive correlation with the dissolved and sedimentary metal concentration also augmented this possibility.

At this site, Zn showed enrichment in sediments relative to the particulate matter only during the monsoon period. In the non-monsoon periods and especially during the postmonsoon season, Zn showed high concentration in the particulate fraction. In the suspended sediments of the Godavary River, India also, Biksham et al. (1991) found that Zn was enriched in particulates by a factor of 3-15 times than the bed sediments. They have related this to the finer nature of the suspended particles with multiple hydroxide coatings, which can efficiently adsorb metals. Sediment resuspension may partly explain the elevated particulate metal concentration in this season.

Zn exhibited high correlation with organic matter at this site (Table C.12). Sediment humic substances have high ability to complex with metals. According to Hong et al. (1994), Zn has moderate binding capacity with humic and fulvic acids and they observed that 93-98 percentage of Zn was complexed by organic matter in the interstitial water as a result of high ligand concentration. None of the hydrographical parameters exhibited correlation with the metal indicating its anthropogenic source (Table C.3). Zn showed highly significant positive correlation with Cd and Pb at this site. Since neither these two metals have a biogenic origin, association of Zn with them points to the anthropogenic source, presumably industrial effluents.

In a study on the modern deltaic sediments of the Cuaverry River, Seralathan (1987) found that Zn was highest at the river channel rather than in the tidal channel, swamps or marine sediments. Here, Zn varied between 80-170 ppm. However, in the Vellar River, concentrations were lower than that of the estuary (Mohan, 1997). Joseph (2001) reported Zn in the Chitrapuzha river sediments in the range 137.89 to 352.1mg/kg.

At the estuarine site, Zn recorded the highest concentration among all metals studied except Fe. Zn ranged from 47.64 to 106.1μg/g with an annual mean value of 70.01μg/g. The minimum concentration was recorded during the postmonsoon season, while the monsoon and premonsoon periods exhibited almost similar
Trace Metals

concentration ranges. Zn was found to be present in higher concentration in the estuarine sediments than the river sediments (Mohan, 1997). In the present study, except for Zn, the river sediments were found to be enriched with all other metals relative to the estuarine sediments. The high concentration of Zn in the estuary can be related to the precipitation of Fe and Mn hydroxides to which Zn is adsorbed, which are high in the estuarine environment than in the river.

Zn exhibited significant correlation with Mn at this site (Table C.10). This indicates its probable association with Mn hydroxide in the transport to the estuary and co-precipitation with the hydroxide therein. The major source of sedimentary Zn in this estuary may be the rivers draining into it. Various chemical industries and in particular, a Zn refining factory is located on the banks of the Periyar River, which drain into this estuary. In addition to this, emanations from boats and ships are other possible source for Zn. The sacrificial anodes made up of Zn and the zinc chromate paint used in boats both may be significantly contributing to the Zn pool of this estuary. The low seasonal variation also points to this consistent source. Resuspension of sediments in the postmonsoon season may have facilitated desorption of the metal from the sediment and subsequently, increased the particulate metal levels. The enrichment of the metal in the particulate matter relative to sediments is a testimony to this.

Among the hydrographical parameters, dissolved oxygen showed a negative relationship with Zn (Table C.3). This indicates the increased precipitation of the metal as sulphides as dissolved oxygen level decreases. Zn was found to be correlated neither with the organic matter nor with the finer fraction of the sediment at this site. Therefore, diagenetic enrichment may not be feasible for this metal and thus, points to the purely anthropogenic sources.

In a study by Krishnakumar et al. (1998) Zn showed a concentration value of 68.8μg/g in the sediments collected from the vicinity of a chemical and fertilizer factory. In the Beypore estuary, Kerala, enrichment of Zn towards the bar mouth of the estuary was observed. Here, Zn varied between 25 to 75 ppm. In a previous study on the Cochin estuary, Joseph (2001) reported Zn in the range 23.52-271.25mg/kg. The present observations were in line with those reported in earlier studies.
Copper

In the aquatic environment, copper occurs in many organic and inorganic forms. After entry into the aquatic system, Cu may remain dissolved or adsorbed onto particulates, sink to the sediments or be absorbed by organisms. Sediments are regarded as an important sink for the removal of Cu. Excess Cu from the water may get adsorbed onto particulates and settle to bottom sediments. If water is depleted of the metal, the adsorbed Cu may re-dissolve or desorb to increase its concentration in the interstitial waters. Thus sediments are involved in determining the fate of Cu in the aquatic environment.

Cu, in this study, exhibited comparable concentration in the mangrove and riverine locations, whereas the estuarine sediments recorded remarkably low concentration. Seasonal distribution of the metal too was quite unique for each site (Figure 5.22). Mangalavanam (station 1) displayed Cu in the range 4.780-52.38μg/g, while, the other mangrove site, the ‘Fisheries’ station recorded Cu in the range, 12.10-30.93μg/g. Chitrapuzha, the riverine site showed Cu in the range 3.848-40.49μg/g, whereas in the estuarine sediments Cu varied from 3.357-16.00μg/g (Table A. 52). The highest annual mean concentration was recorded at station 1 closely followed by station 3 and station 2.

Among the two mangrove habitats analyzed, station 1 was found to have high sediment Cu content than station 2. Seasonal distribution was different for the two stations. Monsoon season was characterized by peak concentration at station 1 and with a minimum in the postmonsoon period. However, at station 2, such distinct seasonal variation was difficult to observe. Slightly higher values were seen during the postmonsoon period.
Forstner et al. (1989) observed Cu to be present in large quantity in sediments in the anoxic condition than in oxic condition. In the anoxic sediments sulphides of Cu are found to be more stable (Haraldson and Westerlund, 1988). Tam and Wong (1996) have further shown that sulphide precipitation is very important in mangrove sediments. Low redox potential in the mangrove sediments indicates the presence of significant quantities of H₂S that precipitates metals in insoluble sulphide forms (Huerta-Diaz and Morse, 1992). Hence the elevated Cu concentration in the mangrove sediments may be due to the increased precipitation of the metal as insoluble sulphides.

At both the sites, Cu exhibited an inverse relationship with dissolved oxygen (Table C.3). This clearly shows precipitation and incorporation of Cu into sediments. In the mangroves, oxygen is used up by the microbial community for the remineralization of organic matter eventually resulting in oxygen depletion in the sediments, creating ideal condition for bacterial sulphate reduction (Berner, 1983). The metal in this reduced environment may combine with sulphides forming stable metal sulphides. The simultaneous decrease in dissolved Cu may be an indication of its association with particulates and subsequent settling to sediments as Cu sulphides with decrease in dissolved oxygen levels. Haraldson and Westerlund (1988) also observed a rapid decrease in dissolved Cu in the anoxic zones of the Black Sea and Fram Varren fjord, Norway. However, at station 2, pH was found to be influencing Cu concentration (Table C.3).

At both the mangrove habitats, Cu did not show any significant correlation with sedimentary organic carbon (Table C.12). Such behaviour was reported earlier
in the anoxic condition for Cu (Haraldson and Westerlund, 1988; Seralathan, 1987). They have reached in the conclusion that all organic compounds are not capable of complexing with Cu and that therefore total organic carbon measurements cannot be a good indicator of Cu complexing capacity. Another reason may be the non-availability of traces for concentration for Cu due to the presence of huge amount of organic matter in the mangroves. Sediments can be exposed to continuous disturbances such as bioturbation and resuspension, which can mark changes over small time span. Thus the non-correlation with sedimentary organic carbon may indicate other anthropogenic sources of this metal (Helland et al., 2002). Cu was found to be enriched in the finer fraction of the sediments in this study (Table C.3). Excellent correlation with finer components of the sediments points to the increased adsorption of the metal facilitated by the greater surface area of the particles.

Cu exhibited remarkably high correlation with other metals such as Fe, Zn, Co and Pb at station 1 (Table C.10). However, at station 2, significant correlation was observed only with Cr. High correlation with Fe indicates that Cu is associated with Fe oxyhydroxides rather than Mn hydroxides. Shaw et al. (1990) pointed out that Cu is enriched in the sediments by transport with detrital biogenic material followed by adsorption onto sediments. Zn also is reported to have a biogenic origin. The excellent correlation exhibited by both the elements (Table C.10) reflects that they have a common source in these mangroves. Since at station 2, Cu correlated only with Cr, Cu can have other sources such as anthropogenic inputs.

In this study, particulate fraction showed higher concentration than the sediments. Thus, it can be inferred that Cu is enriched in the particulate matter rather than the sediments in these mangrove environments. The intense bioturbation occurring in the mangroves changes the chemistry of the sediments significantly. Animals can manipulate the sediment texture as they burrow into them. Substantial amount of particulate matter is created when they feed or burrow. Thus the observed depletion of Cu in sediments can be related to the bioturbative or bio-irrigative processes operating in the mangroves.

The concentration of sedimentary Cu reported in this study was much lower than those reported earlier. Badarudeen (1997) reported Cu in the range 15-91ppm
in Cochin mangroves. Cu, in the Brazilian mangroves ranged from 18-80\(\mu g/g\) (Machado et al., 2002), whereas the Mai Po mangroves, Hong Kong, recorded Cu in the range 51-87\(\mu g/g\). In a study by Seralathan (1987) on the Cauvery mangroves, Cu was found to vary in a small range, i.e., from 70 to 78 ppm.

In the river sediments, Cu varied from 3.848 to 40.49\(\mu g/g\). Here, the monsoon period was characterized by the highest concentration and the minimum was recorded during the postmonsoon season. The main source of Cu in this river may be the industrial effluents. Use of Cu as catalyst in many industrial processes result in large inputs of the metal into the aquatic environments (Moore and Ramamoorthy, 1992). Since Cu is an efficient biocide, urban runoff may also contain high metal content.

At this site also, Cu was found to be enriched in the particulate fraction. This might be due to the resuspension processes occurring in this season. Since the maximum concentration was observed in the rainy season, the main source of Cu into this system may be the runoff water. The heavy influx of freshwater might have leached the metal-rich particles from the effluent discharge points elevating the metal load in the monsoon season. During the summer season, stream flow is greatly reduced and during this season, the riverbed may absorb trace metals discharged from untreated/partially treated domestic and industrial wastes. Immediately after the heavy rain, trace metals from the river sediments are released to the overlying water by resuspension and discharged to the estuarine environment. The presence of higher Cu concentration in the particulate fraction during the non-monsoon period may be the result of the resuspension process. Biksham et al. (1991) also found enrichment of Cu in the suspended sediments of the Godavary River, India, by a factor of 2-4 times than the bed sediments. He has related this to the finer nature of the sediments, which are rich in multiple hydroxide coating thus facilitating increased metal adsorption.

Cu, at this site, showed remarkably high correlation with sedimentary organic carbon and with the silt and clay fraction of the sediment (Table C.3, C.10). Humic materials of freshwater are reported to bind >90 percentage of dissolved Cu, whereas those in seawater bind only 10 percentage of total Cu (Mantoura et al., 1978). According to the Irving-Williams series, Cu shows
highest affinity for humic substances except Hg. Forstner et al. (1989) have further shown that Cu complexation with organic matter has a dominant role in the transfer of the metal to biologically inactive form. The strong correlation with the muddy fraction reflects the increased adsorbing capacity of the clay mineral particles (Table C.3). In the Vellar River, Mohan (1997) observed higher Cu content in the river than the estuary and related this to the high amount of fine sized particles.

Among the hydrographical parameters, only pH correlated with Cu at this site (Table C.3). Complexation with humic substances was found to be highly pH dependent, and in addition to this, sedimentary organic carbon also was found to have good positive relation with Cu (Table C.12). Thus, with increasing pH, adsorption of Cu onto humic substances might have increased. Cu exhibited correlation with Fe, Co and Ni in this river indicating a common source of these metals (Table C.10). Association with Fe indicates that Cu may have coprecipitated with Fe oxides rather than with Mn oxides.

The estuarine sediments showed remarkably low Cu concentration. Here, the premonsoon season recorded the maximum concentration and the minimum was observed during the postmonsoon period. Considerable dilution of the metal-rich fluvial sediments by the metal-deficient marine sediments might have occurred reducing the metal content. The sand dominance of the substratum can also be a reason for the low metal content. Sand particles are well known for their poor capacity to hold metals onto them and hence, even though flocculation of Fe and Mn oxides, to which Cu is preferably attached, occur in the estuary, they are exported to the sea by waves and currents. Another reason for the general reduction of the metal in estuaries is desorption of the metal adsorbed onto clay minerals when river water mixes with seawater. In a study by Helland (2001) in a microtidal estuary, only a small amount of Cu was associated with particles and settled out. The low entrapment of the metal suggested that bulk of the metal stayed complexed, probably with humic substances and was transported out of the estuary.

Cu finds its way to this estuary mainly through anthropogenic inputs. Cu is used as a catalyst in many industrial processes, which has led to large inputs of Cu into the marine environment. Relatively high concentration of Cu was observed in the sediments collected from Thannirbavi River, Mangalore, from the vicinity of
effluent discharge point of a chemical and fertilizer factory (Krishnakumar et al., 1998). Since various industries release their effluent load directly or indirectly to the Cochin estuarine system, Cu contamination is indeed possible. In addition to this, since Cu is an efficient biocide, it is used as antifouling paints in boats and ships. The intense boat traffic in the estuary may also have contributed considerable amounts of Cu to the estuarine sediments. The observed non-correlation of the metal with hydrographical parameters also points to its anthropogenic sources.

At the estuarine site, Cu was positively correlated with organic carbon and with the finer fraction of the sediment (Table C.12, C.3). Cu is well known for its complexation capacity with organic compounds especially with humic substances. According to Moore and Ramamoorthy (1992), among the humic substances of different origin, marine sedimentary humic and fulvic acids have the greatest ability to form stable complexes with Cu. Another possible mechanism for this observed covariance is the exchange reactions between clay minerals and the metal ions. Organic flocculent coatings on sediment particles also greatly affect the adsorption capacity for trace metals. Thus, metal association of sedimentary organic carbon suggests strong interaction of the metal ion with organic matter, which, in turn, is further concentrated by adsorption onto clays. Such a close relationship of Cu with total organic carbon was reported by many authors (Qu and Kelderman, 2001; Piatina and Hering, 2000; Monterrosso et al., 2003; Fan et al., 2002; Nair and Ramachandran, 2002; Li et al., 2001; Wang et al., 1997; Fu et al., 1992).

Cu, in this estuary, exhibited significant positive correlation with Fe, Co, and Cd (Table C.10). Correlation with Fe points to the association of the metal with Fe oxyhydroxides. Significant correlation with other metals indicates that there may by common sources or at least one single major source of these metals in this estuary. In a previous study by Joseph (2001), Cu was reported to vary from 11.8 to 37.09 mg/kg in the Cochin estuary. These values were higher than those in the present study. However, in the Beypore estuary, Kerala, Cu ranged from 2-17ppm (Nair and Ramachandran, 2002).
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> Cobalt

Cobalt is an essential element to biological systems and is also toxic at quite low concentrations (Ghatak et al., 2002). Anthropogenic input of Co is through the usage of fertilizers and the deposition pattern indicates enrichment in soils (Young, 1979). In this study, Co recorded highest annual mean concentration at station 2, the mangrove site. The order of abundance of the metal was station 2 > station 3 > station 1 > station R. Generally, estuarine sediments was characterized by low metal content. Seasonally, monsoon period was observed with maximum concentration at the river and mangrove sites (Figure 5.23). Premonsoon period recorded the highest concentration at the estuarine site. Except at station 2, minimum concentration was observed during the postmonsoon period.

![Seasonal mean variation of sedimentary cobalt](image)

Figure 5.23: Seasonal mean variation of sedimentary cobalt

In the present study, the mangrove sediments were characterized by high Co content. Of the two mangrove habitats, the 'Fisheries station' (station 2) recorded higher concentration. Co varied from 12.44 to 26.30µg/g at this site, whereas at station 1, a wider range was observed (4.630-23.01µg/g) (Table A.53).

Mangrove ecosystems have the capacity to act as sink or buffer and remove or immobilize trace metals before they reach nearby aquatic environments (Harbison, 1986). Because the sediments have a high proportion of fine particles, high organic content and low pH, they effectively trap trace metals often by immobilizing them in the anaerobic sediments either by adsorption on ion exchange sites of sediment particles, incorporation into lattice structures of the clay particles or precipitation as
insoluble sulphides (Harbison, 1986; Macfarlane and Burchett, 2001). Mangrove ecosystems, although possessing enormous ecological and commercial importance, are often subject to effluent discharges, urban and agricultural runoff and solid waste dumping, due to the proximity to urban development (Macfurlane, 2002). Since Co has a significant anthropogenic origin elevated concentration observed in the mangroves may be due from the runoff waters.

Microbial degradation of the high content of organic matter in mangrove muds generally removes all oxygen from sediments below the surface layer, creating ideal condition for bacterial sulphate reduction (Berner, 1983). Metals dissolved in this water as free ions or as metal-humate complexes are then deposited as sulphides. Co showed significant negative correlation with dissolved oxygen at both the mangrove habitats. This clearly shows the reductive precipitation of the metal. As dissolved oxygen decreases, H₂S production is enhanced facilitating the precipitation of the metal as sulphides.

Ghatak et al. (2002) have shown that humic substances play an important role both in the inactivation of toxicity and the mobilization/immobilization process of Co. They have also found that fulvic acid-Co complexes are much stable than the humic acid-Co complexes. Since humic substances were found to be present in great concentrations in the mangroves, Co may have got associated with them. The highly significant positive correlation observed between the metal and organic matter in the present study also indicates the metal-humic acid complexation in the sediments (Table C.12). At station 1, Co exhibited significant positive correlation with almost all the metals studied. This shows their common sink in the sediments. However, at station 2, Co displayed correlation only with Pb indicating the anthropogenic source of the metal at this site.

During the monsoon period, both the sites recorded maximum concentration indicating that the main pathway for the metal was through the runoff water. The finer sediments brought in by the heavy influx of freshwater may have got trapped in the tangled network of mangrove roots thus elevating the net metal concentration. At station 1, sediments recorded lowest concentration during the postmonsoon period, whereas the particulate metal concentration was highest
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during the same period. Resuspension processes may be the reason for this depletion of metal in this period. However, no such particulate matter enrichment was observed at station 2.

At the riverine site, Co varied from 3.341 µg/g to 24.90 µg/g. Monsoon period showed highest concentration and the minimum was observed in the postmonsoon season. Here, Co was found to be highly enriched in the finer sediments and organic carbon also showed positive correlation with Co (Table C.3, C.12). Both these observations clearly point to the association of Co with complexing polymeric molecules such as humic substances. Ghatak et al. (2002) also observed high affinity of Co for humic complexes. Another significant source of Co may be the industrial effluents.

Among the hydrographical parameters, only pH was found to have any influence on Co distribution (Table C.3). Metal-humic acid complexation is largely influenced by the change in pH (Moore and Ramamoorthy, 1992). Co, that may be associated with Fe and Mn oxides, is also found to precipitate at higher pH. Moreover, co-precipitation of Co with Fe and Mn oxides is reported (Zhang et al., 2002; Hamilton-Taylor et al., 1999; Lienemann et al., 1997; Moffett and Ho, 1996; Ozturk, 1995; Balistrieri et al., 1994; Shaw, et al., 1990; Jacobs et al., 1985). Thus the covariation of Co with pH may either be due to its complexation with sedimentary humic substances or due to increased precipitation of Fe and Mn oxides. In contrast with most of the metals studied, Co did not show any preference for the particulate matter at this site. Hence, it could be inferred that Co that may have entered the system either in the soluble or particulate form were rapidly incorporated to the sediment with limited release from them.

In this study, Co showed positive, though less significant correlation with Fe. However, highly significant correlation was observed with Cu and Ni (Table C10). Thus the close linear relationship between these metals points to their common fate in this aquatic system.

In the estuarine sediments, Co was present in very low concentrations ranging from 2.256 to 11.90 µg/g. Premonsoon season was characterized by a concentration
hike, while a minimum was observed during the postmonsoon period. A general decrease in Co concentration at the estuarine mouth was reported by Seralathan (1987) in the Cauvery delta sediments. He has related this general decrease to the desorption of Co, which may be concentrated in freshwater clay minerals or as due to the partial removal of the element from Fe and Mn oxides. However, a contrasting behaviour of Co was reported in the Vellar estuary (Mohan, 1997). Here, Co showed high content in the estuarine sediments than the river sediments.

Seasonally, Co exhibited highest concentration in the premonsoon period. This may be due to the increased co-precipitation of the metal with Fe and Mn oxyhydroxides, with increasing seawater cations. A corresponding decrease in the particulate metal concentration was also observed during the same period. In addition to this, Co co-varied with Fe. Considering all these facts, it can be inferred that Co was mainly associated with Fe oxides and hydroxides, which would have get precipitated with increasing salinity. Association of Co with Fe was observed in the Chennai estuaries, east coast of India, in a study by Achyuthan et al. (2002). In the present study, the observed reduced metal levels in the postmonsoon period can be due to the resuspension process occurring in the estuary. Particulate metal concentration showed a hike during this period augmenting the possible resuspension process.

The general lower concentration of the metal in the estuary can be due to the sandy nature of the substratum. However, Co was enriched in the clay fraction of the sediment and though less significantly, the element correlated positively with organic matter. The co-variance of Co with metals like Cu and Ni indicates their similar fate in the estuarine sediments.

Co varied from 11 to 35 ppm in the Beypore estuary, southwest coast of India, in a study by Nair and Ramachandran (2002). Joseph (2001) reported Co concentration in the range 6.7 to 20.92 mg/kg in the Cochin estuary. Co was found to vary from 3 to 12 µg/g in the sediments of Gulf of Mannar, India (Jonathan and Ram Mohan, 2003). The concentration of Co observed in the present study was similar to that reported earlier.
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> Chromium

Chromium chemistry in aquatic environments is complex since many individually or simultaneously occurring reactions or processes can affect its chemical behaviour. Important among these are oxidation-reduction, precipitation or dissolution of a solid phase, adsorption or desorption of Cr in saline water, chemical speciation and biological interactions. The equilibrium tendencies of all these reactions regulate concentration and chemical behaviour of Cr in aquatic systems. Irrespective of the scavenging processes, sediments are considered as the ultimate sink for Cr in the aquatic systems (Sadiq, 1992a).

Cr concentrations showed wide variations in each of the aquatic systems analyzed. The highest annual mean concentration was recorded in the mangrove sediments (station 2). Station 1, which is also a mangrove site and the river sediments recorded similar concentrations, while the estuarine sediments exhibited much lower Cr content. The order of abundance of the metal was station 2 > station 3 > station 1 > station R. Seasonal variation of dissolved chromium is depicted in Figure 5.24.

At Mangalavanam (station 1), Cr varied from 23.65-96.65 μg/g whereas at station 2 (Fisheries station), the concentration range was 40.83 to 114.8 μg/g. River sediments showed Cr content in the range 26.93-117.94 μg/g, while, Cr ranged from 22.97 to 48.70 μg/g in the estuary (Table A.54). Seasonally, premonsoon season was characterized by highest Cr content at all stations except at station 2. Here, postmonsoon period recorded the highest concentration. Sedimentary Cr showed lowest metal concentration during the monsoon period in both the river and estuary. At Mangalavanam (station 1), minimum concentration was observed in the postmonsoon season while, the monsoon and premonsoon seasons showed very slight variation at station 2. ANOVA calculations also showed highly significant variation between the stations (Table B.8).
One of the most important factors for determining the valence state of Cr in natural waters is the oxygen content and redox potential of water. Concentration of Cr (III), which is the insoluble form, increased rapidly under reducing conditions (Florence and Batley, 1980). Concentrations of total dissolved Cr and Cr adsorbed on particles both reduced rapidly at the $O_2$-$H_2S$ interface (Emerson, 1979). Annual mean concentration was higher at station 2 than at station 1 among the mangroves. Since sampling was done in the vegetated area at station 1, interactions of fine roots of plants would have altered the sediment chemistry by creating oxic microenvironments. In this condition, Cr (III) is rapidly oxidized to the soluble form. Since intense anoxic conditions existed in the bulk sediments collected at station 2, Cr would be preferably remained in the sediments. Amdurer et al. (1983) have further shown that the residence time of Cr$^{3+}$ is much lower than Cr$^{6+}$ in the water column and is therefore, gets rapidly incorporated into the sediments.

Cr exhibited excellent correlation with pH at station 1 (Table C.3). Cr was found to be correlated well with organic matter also (Table C.12). These correlations point to the association of Cr with humic or fulvic acids, which are the dominant fraction of the sedimentary organic matter. Cr (III) is strongly sorbed on humic acids and the adsorption increases with increasing pH of the media. In the present study also pH was found to have high influence on Cr distribution (Table C.3). Cr also showed high correlation with Mn at this site (Table C.10). This indicates association of Cr with Mn hydroxides. In a study by Ong Che (1999) in the mangroves of Mai Po, Hong Kong, Cr showed highly significant correlation with Mn. This was attributed to the
diagenetic processes associated with Mn, which mobilized a significant fraction of Cr. Co-variance of Cr with other toxic metals like Ni and Cd shows the similar geochemical processes undergone by these metals.

However, station 2, even though a mangrove site, presented a completely different picture. Cr exhibited poor correlation with organic matter, yet, it was enriched in fine sediments. Correlation with pH was also found to be less significant, although positive. Cr showed an inverse relationship with Mn. Velde et al. (2003) also observed non-correlation of Cr with Mn in the American and French salt marshes. This can be related to the redox nature of Cr. Cr$^{6+}$ is easily reduced by dissolved ferrous sulphides and by certain organic compounds with sulphydryl groups. In contrast to this, Cr$^{3+}$ is oxidized rapidly by a large excess of MnO$_2$. Since Cr (VI) is the soluble form, with increasing Mn, release of sediment bound Cr (VI) may also have enhanced.

In the river, Chitrapuzha (station 3), Cr varied from 26.93 to 117.94μg/g. Here, postmonsoon season recorded the maximum concentration, while monsoon exhibited lowest metal content. Cr has wide industrial applications and is extensively used in plating industry and in paints. Hence the enormous quantity of the metal reaching the aquatic environment finally settles in the sediments. Apart from this industrial sources, municipal wastewaters release considerable amount of Cr (Moore and Ramamoorthy, 1992). In freshwaters, anthropogenically introduced soluble Cr (VI) is removed by reduction to Cr (III) and is precipitated. Hence, Cr is transported in rivers primarily in the solid phase. The premonsoon season recorded the maximum concentration of Cr at this site. During summer, when stream flow is considerably reduced, effluents from industries are released without much treatment to the river. The river sediments act as the ready reservoir for these effluents and accumulate large quantity of the metal in the sediments. The observed non-correlation of Cr with hydrographical parameters also points to its anthropogenic source (Table C.3).

Of the metals studied, Cr was the only one, which showed no significant correlation with any other metal indicating the distinctly different geochemical processes undergone by the metal. The dissolved fraction of the metal was found to increase as the sedimentary concentration diminished. This can be due to the
differential solubility of the element in different chemical environments. Cr did not show any affinity either towards organic matter or to the finer sediments.

At the estuarine site, Cr ranged from 2.35 to 48.70μg/g. Comparing with other aquatic systems under study, estuarine sediments showed much low Cr content. In fact, the concentrations were half of that observed at the river site. The general reduction in concentration can be attributed to the nature of the substratum and the hydrodynamic features of the area. The sand particles dominant in the estuarine sediment show little affinity for trace metals and due to the high tidal activity dilution by metal-impoverished marine sediments were also possible.

Seasonally, premonsoon recorded the highest concentration, while the minimum was observed during monsoon. Cr was found to be associated with Fe and Mn hydroxides. Many authors have pointed out the transport of the metals associated with these hydroxides in freshwaters (Velde et al., 2003; Seralathan, 1987; Mohan, 1997; Nair and Ramachandran, 2002). Flocculation and subsequent precipitation of these hydroxides in the estuarine environment was found to increase the concentration of the adsorbed metals also (Evans and Cutshall, 1973). Among the hydrographical parameters, both salinity and temperature showed significant positive correlation with Cr in this study (Table C.3). This clearly shows the increased precipitation of Fe and Mn hydroxides to which the metal is attached with increasing salinity. Cr exhibited high correlation with organic matter and with the fine sediment fractions. Apart from the surface area related enrichment of the metal, cation exchange capacity of sediments and affinity of metal ions for different types of clay minerals also contribute substantially to the metal-fine fraction proportionality of sediments.

The higher concentration observed during the non-monsoon period may be due to the increased adsorption of the metal to the particles facilitated by the longer residence time of the particles in the water column. Because of its industrial applications, anthropogenic inputs, especially from industrial effluents, are regarded as the major contaminant source of Cr in the marine environment (Nriagu and Nieboer, 1980). Since many industries are located near the estuary, contamination from the effluent discharges is a distinct possibility. Moreover, municipal wastewaters are reported to contain substantial portions of Cr (Moore
and Ramamoorthy, 1992). Thus considerable amount of Cr found in this estuary could be traced to the effluent and sewage discharges. Apart from these sources, leakages from boats may also introduce Cr to this estuary since the paints used in boats have high Cr content.

Nickel

Nickel is not a wide spread or significant contaminant of most freshwater and marine sediments (Moore and Ramamoorthy, 1992). Ni enrichment of nearshore sediments reflects anthropogenic inputs from industrial and municipal discharges and other sources such as urban storm water run off and sludge disposals.

In this study, Ni exhibited highest annual mean concentration in one of the mangrove environments. The lowest Ni concentration was observed in the estuary. At station 1, Ni ranged from 8.224 to 71.15 µg/g, whereas station 2, which is also a mangrove habitat, recorded much high level. Here, Ni varied from 40.61 to 86.82 µg/g. The polluted river sediments showed Ni in the range 13.21 to 73.44 µg/g and in the estuarine sediments, Ni was found to vary from 9.101 to 31.10 µg/g (Table A.55).

![Figure 5.25: Seasonal mean variation of sedimentary nickel](image)

Of the two mangrove habitats, station 2 showed distinctly higher Ni content than station 1. Seasonally, the two stations behaved quite differently. Postmonsoon season recorded lowest concentration at station 1, while at station 2, this season showed the maximum concentration. The monsoon and premonsoon seasons
showed little variation in Ni content at station 1. During the premonsoon period, Ni concentration in the sediments was lowest at station 2 (Figure 5.25).

Sediments are known to accumulate metals in several orders of magnitude more than water. Only very small amounts of metal are bio-available to plants, and in the mangroves, a large proportion is precipitated as sulphides in the sediments. Due to the enormous load of organic matter in the mangroves and the intense microbial degradation often result in permanent anoxic condition in the mangroves. Reduced sediments are found to accumulate more Ni (Lacerda and Abrado, 1984; Lacerda et al., 1991). Dissolved Ni is also found to decrease under anoxic condition (Lu and Chen, 1977). Ni$^{2+}$ ion is found to form stable complexes with organic and inorganic ligands. Inorganic complexing ligands include halides, sulphates etc. Organic ligands with oxygen, nitrogen, and especially sulphur donor atoms form strong complexes with Ni (Moore and Ramamoorthy, 1992). Due to the intense sulphate reduction occurring in the mangroves, H$_2$S is released from the sediments and Ni forms strong complexes with the sulphides (Tam and Wong, 1996; Huerta-Diaz and Morse, 1992). Precipitation of Ni as sulphides may be the reason for the observed high concentration of Ni in the mangrove sediments.

Ni was found to be enriched in the humic and fulvic acids and in a study by Nriagu and Coker (1980), 10 percentage of the total Ni was bound to the organic matter. According to Moore and Ramamoorthy (1992), complexes of Ni with humic or fulvic acids are of moderate stability. Since, humic substances were abundant in the mangroves under study, complexation with them would have increased the Ni content in the sediments.

Among the hydrographical parameters, Ni showed significant positive correlation with pH, while, dissolved oxygen showed an inverse, though less significant correlation (Table C.3). Complexation of Ni with humic or fulvic acids are found to increase with pH. At both the sites Ni showed highly significant correlation with organic carbon also. Thus, complexation with sedimentary humic substances may partly explain for the elevated metal content at this site.

Ni exhibited significantly high correlation with Mn and Co and moderately strong relationship with Fe, Cr, and Cu at station 1 (Table C.10). Good correlation with Ni and Mn was reported earlier (Luminez and Paes-Ozuna, 2001). They
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related this association to the peculiarities in Mn cycling. When reducing conditions are dominant as in the mangrove sediments, soluble Mn is the dominant form migrating through the pore water to the overlying water column. When oxidizing conditions predominate, Mn is present in solid form, which is retained in the sediment column. Thus, the resuspension-deposition pattern of Mn affects the mobilization of other metals (Shaw et al., 1990; Huerta-Diaz and Morse, 1992). Correlation with other metals denotes the common sink for these metals in the mangrove sediments. Several authors (Forstner and Wittman, 1981; Sing and Subramanian, 1984) have reported the role of sediments as the sink for trace metals. However, at station 2, Ni showed significant correlation only with Zn and moderately with Cu.

Seasonally, station 1 recorded lowest concentration during the postmonsoon period. Resuspension of fine sediments, which are rich in metals, may be the reason for this low metal content in the sediments. Intense reducing condition, facilitated by the increased rate of evapo-transpiration during the summer periods would have resulted in elevated concentration of the metal in the premonsoon season. However, this trend was reversed at station 2. Here, postmonsoon season recorded the maximum concentration and premonsoon, the minimum. The finer fraction of the sediment brought in by the monsoon runoff starts to settle in the quieter postmonsoon period in the creek waters resulting in elevated metal concentration. Ni is found to have affinity for inorganic ligand like Cl⁻ (Moore and Ramamoorthy, 1992). In the premonsoon season, as the chloride concentration increases, sediment-bound Ni is released as they form chloride complexes.

In a study by Saifulla et al. (2002) on the mangrove sediments of the Indus Delta, Ni concentration in the sediments was very high (48.3 to 71.2μg/g) when compared to the water. They have attributed the high concentration in sediments to the clayey loam texture of the sediments with relatively high silt and clay fraction, which are known to bind heavy metals. However, in the mangrove sediments of the Cauvery Delta, Ni varied from 85 to 156 ppm. Ni, in the mangrove sediments elsewhere, showed wide variation in concentration. In the Mai Po mangroves, Ni was present in the range 44-87μg/g (Ong Che, 1999) whereas the Brazilian mangroves, Machado et al. (2002) recorded Ni in the range, 1.8 to 12.7μg/g.
Chitrapuzha, station 3, recorded Ni in the range 13.21 to 73.44 µg/g. The monsoon season was characterized by the peak concentration and the minimum was observed during the postmonsoon. The major polluting sources for Ni are chemical industries, tanneries, cement, shipyard, and refineries (Khan, 1995). Since, this river receives effluents from various industries, Ni contamination is highly possible here. According to Moore and Ramamoorthy (1992), anthropogenic inputs from municipal discharges, urban storm water runoff and automotive combustion of Ni-containing diesel oil also contribute Ni to the coastal water bodies. The observed non-correlation with hydrographical parameters also augments the possible anthropogenic source in this system. Monsoon season was found to be dominating in Ni content. Metal-rich sediments brought in by the heavy land runoff may be reason for this sudden hike in metal concentration. The observed postmonsoon minimum can be attributed to the resuspension of sediments occurring in this season. A corresponding increase in particulate metal concentration in the same season emphasizes the possibility for the resuspension process.

Ni showed high correlation with Fe in this river sediment. Association of Ni with Fe and Mn hydroxides are widely recognized. According to Moore and Ramamoorthy (1992), association of Ni with Fe and Mn oxides is an important mode of transport for the metal. In a study by Ambatsian et al. (1997), it was shown that Ni was transported from the land with Mn oxides but was released to water and a major fraction of this was associated with Fe oxides in the sediment. Nair and Ramachandran (2002) related the strong positive relationship to the sorbing or co-precipitation of the metal onto Fe and Mn oxyhydroxides. Metals like Cu and Co also correlated with Ni (Table C.10). Hence it can be inferred that for these elements, Fe oxides are the major adsorbents rather than Mn oxides in this river.

Ni showed enrichment in the fine sediments and this may be due to the increased specific surface area and due to the ion exchange capacity of the clay particles. This clearly shows the size control of the sediment over Ni concentration. Moderate correlation with organic matter shows the complexation of the metal with humic substances present in the sediment.

Considerably low metal content characterized the estuarine sediments. Here, the variation was from 9.101 to 30.10 µg/g. Premonsoon season recorded the peak
concentration, while little variation was seen between the monsoon and postmonsoon concentrations. Low metal concentration at this site can be related to the general textural characteristics of the sediments. Sand dominating sediments have poor ability to hold pollutants onto them and due to the high tidal activity; considerable dilution of the metal by metal-deficient marine sediments is possible.

Seasonally, premonsoon recorded the maximum concentration. Since Fe and Mn oxides are the chief carriers of Ni in the fresh water, increasing salinity would result in their flocculation and subsequent incorporation into sediments. In addition to this, Ni showed highly significant correlation with salinity and Fe at this site (Table C.3, C.10). Thus salinity induced co-precipitation of Fe oxyhydroxides seems to be the major mechanism controlling the Ni cycle of this estuary.

In a study by Nair and Ramachandran (2002) in the Baypore estuary, Ni concentration was found to increase from upstream to bar mouth of the estuary. Mohan (1997) also reported that the Vellar estuarine sediments registered higher concentration than the river sediments. They have related this to the complexation with organic matter, since, according to the Irving-Williams series, after Cu and Hg, Ni forms stable complexes with humic substances. Since surface area of fine particles are high, adsorption onto them take place very efficiently in aquatic systems. In addition to this, cation exchange capacity of sediments and affinity of the metal ions for different types of clay surfaces also contribute substantially to the metal-fine fraction proportionality of sediments. In this study also, Ni exhibited high positive relationship with organic matter and fine silt fraction of the sediments. Ni exhibited remarkably high correlation with other metals such as Cu, Co and Cr indicating a common fate for these metals.

The main source of Ni to this estuary is the industrial effluent discharged to the adjoining rivers. Emanations from Ni containing diesel oil from intense boat traffic may have contributed a substantial portion of the metal. In the Cauvery River estuary, Ni was found to vary from 96 to 156ppm (Seralathan, 1987), whereas in the Baypore estuary, Kerala, Ni varied from 25-98ppm (Nair and Ramachandran. 2002). In the nearby Kayamkulam estuary, Unnikrishnan (2000) noted Ni in the range 8.89 to 91.55 mg/kg. In a previous study by Joseph (2001) in the Cochin estuary, Ni was found to vary between 38.54 to 92.70mg/kg. In the
present study, considerably lower concentration of the metal was observed in the estuarine sediments.

**Cadmium**

Cadmium is probably the most bio-toxic element and is regarded as the priority pollutant. It is widely used in various industrial products and processes. Because of its wide variety of use, anthropogenic inputs into aquatic environments are considered as a principal source of Cd contamination. It is therefore expected that human activities in the estuarine and coastal areas may result in relatively high concentration of Cd (Sadiq, 1992 b). In general, Cd enters the aquatic environments via atmospheric deposition and through effluent discharges from point sources in nearshore areas (Nnagu, 1980).

Among the trace metals studied, Cd showed lowest concentration in sediments at all sites. However, seasonal distribution was different at each site. The highest annual mean concentration was recorded in one of the mangrove sites, station 1. Here, Cd ranged from 1.584-8.876µg/g. An abnormally high value was observed in the month of April. At station 2, the mangrove nursery, the concentration range was relatively small. Sediments showed Cd in the range 0.436-2.528µg/g (Table A. 56). If the high value observed at station 1 is excluded as an outlier, then monsoon season displayed highest metal content (Figure 5.26). However, seasonal changes appeared to have little influence on sedimentary Cd dynamics at station 2. Here, in all the three seasons Cd concentration remained similar. At the riverine station, Cd varied from 0.149 to 4.029µg/g, with a monsoon maximum. The non-monsoon periods exhibited similar metal content. Sediments of the estuary recorded the lowest metal content of all the systems under study. Cd varied from 0.437 to 2.700µg/g at this site. Monsoon season dominated in metal content here with a postmonsoon minimum.
In all the three aquatic systems analyzed in this study, Cd was found to be preferably associated with particulate matter, especially during the postmonsoon period. Affinity of Cd for particulate matter was reported in many studies. (Martin and Maybeck, 1979; Martin and Whitefield, 1983; Dyressen and Kremling, 1990; Horowitz et al., 1996; Lead et al., 1999; Ciffroy et al., 2003). Fine clay particles, biogenic materials and numerous organic and inorganic ligands enrich the suspended sediments. Cd remains solely in the +2 oxidation state and has a natural affinity for the negatively charged clay mineral particles and organic matter (Sadiq, 1992b). Adsorption take place rapidly due to the increased stability of the complexes formed. Thus, both physical and chemical factors favour concentration of the metal in particulate matter.

Of the two mangrove environments studied, station 1 recorded higher value in all the three seasons. Generally, Cd is not affected by fluctuations in oxidation-reduction conditions since it remains in the divalent solo oxidation state. In anoxic sediments where pH and pE are very low, there are plenty of sulphides available, and formation of CdS can be anticipated. Luther et al. (1980) speculated on the formation of CdS, while, Salomons et al. (1987) concluded that trace metals like Cd might occur as sulphides in anoxic sediments. Since mangrove sediments are highly anoxic, Cd may precipitate as CdS in the sediments. Lu and Chen (1977) have further shown that dissolved Cd concentration was decreased under reducing conditions. Chemically, Cd is a sulphophilic element.
Sediments serve as important sink for dissolved Cd (Lyons and Fitzgerald, 1980; Santschi et al., 1980). Sadiq (1992 b) has further shown that adsorption is an important removal mechanism for Cd from water. The most important adsorbents are organic matter, hydroxides of Fe and Mn, clays and particles of biogenic minerals. Cd forms moderately stable complexes with organic matter found in natural waters, including amino acids, amino sugars, polysaccharides, hydroxyl and carboxylic acids of aliphatic and aromatic nature etc., which contain suitable donor atoms for complexation with Cd (Moore and Ramamoorthy, 1992). Since the mangrove sediments contain huge amount of plant debris, large varieties of organic compounds are present in them. Hence, complexation with these compounds increases the metal concentration in mangroves. Positive correlation of Cd with organic matter (Table C.12) emphasizes such complexation reactions. However, Cd displayed a negative correlation with organic matter at station 2. In a study by Morrison et al. (2001) Cd showed no correlation with organic matter.

Cd exhibited significant correlation only with Fe at station 2 (Table C.10). This shows that Cd accumulated in sediments through adsorption of freshly precipitated Fe oxides (Mc Corkle and Klinkhammer, 1991). At station 1 no correlation with any other metal was observed indicating the purely anthropogenic origin of the metal. In this study, Cd was not enriched in fine sediments either (Table C.3). Cauwet (1987) also observed little enrichment of Cd onto finer sediments. Thorne and Nickless (1981) reported a weak correlation between Cd and the size of clay particles in the intertidal sediments of the Severn estuary.

Seasonally, except for the high value in April, concentration was generally high in the monsoon season at station 1. The abnormally high value in April can be due to some point discharges, which occurred at the time of sampling. Monsoon hike in concentration can be related to the increase in metal-rich sediments brought in by the run-off waters. Since sediments act as a perfect sink for the metal, immediate settling of dissolved Cd also is highly favoured. However, at station 2, seasonal changes did not exert any influence on metal distribution. According to Sadiq (1992b), if physical or chemical conditions change in a system, sediment-bound Cd may be regenerated to supply the interstitial and overlying waters. Due to this equilibration process, Cd showed little variation with respect to seasonal changes. Temperature exerted significant influence on metal distribution at both
the sites (Table C.3). This may be due to increased evapo-transpiration creating more intense reducing conditions, which in turn, favours the precipitation of the metal as sulphides.

In the river sediments, Cd varied from 0.144 to 4.029 μg/g with a distinct monsoon maximum, while the non-monsoon periods recorded similar concentrations. Cd is widely used in industrial applications and hence anthropogenic inputs are considered as a principal source of the metal to the river sediments. In general, Cd enters the environment through atmospheric deposition and through effluent discharges from point sources near the sampling site. The observed monsoon hike in concentration further strengthens its possible anthropogenic source. Due to the heavy influx of land runoff increased amount of particulate matter as well as suspended solids rich in metal enter the river and settles to the bottom elevating the metal content in sediments. Lower concentration during the summer period can be due to the meagre runoff.

Among the hydrographical parameters, only pH was found to have any influence on Cd distribution (Table C.3). Moore and Ramamoorthy (1992) have shown that adsorption of Cd onto sediments increases with pH and beyond a threshold value (~7) virtually all the metal ions are sorbed. Cd showed moderate correlation with silt and clay fraction of the sediment and this could be related to the adsorption of Cd²⁺ on negatively charged clay mineral particles. Cd, in this study, correlated well with organic matter (Table C.12). Poultron and Simpson (1988) observed an unusually high abundance of organic-bound Cd in Lake Ontario sediments and Rosental et al. (1986) found a strong association between Cd and organic matter of the sediments of the False Bay. In a study by Monterosso et al. (2003) also Cd showed strong positive relationship with organic matter. The metal may interact in solution with dissolved organic matter by complexation or chelation processes that are in turn, concentrated by adsorption onto fine particulates such as clay minerals.

Cd exhibited excellent correlations with Mn, Zn and Pb in these river sediments (Table C.10). Adsorption of Cd onto Mn hydroxides is indicative of its possible co-precipitation with Mn oxyhydroxides. Since Cd and Pb can find their
way to this river through aerial discharges from industrial emanations, their association is highly probable.

Sediments of the estuary recorded low Cd content. Cd ranged from 0.437 to 2.614 µg/g. The low metal content can be related to the sandy nature of the substratum. Palanichamy and Rajendran (2000) in a study on the Gulf of Mannar sediments observed the release of Cd from sediments to the overlying water due to the coarser nature of the sediment.

The main source of Cd in this estuary may be the effluent discharge. Cd is extensively used in at least one of the industries located on the banks of river Periyar, the major river draining into Cochin estuary. Flocculation of Fe and Mn oxides to which a certain portion of Cd is adsorbed is also possible when freshwater mixes with seawater. Excellent correlation exhibited by Cd and Mn also supports this (table C.10). Among the hydrographical parameters, dissolved oxygen showed significant inverse relationship with Cd. When dissolved oxygen levels decline, increased amount of Cd gets precipitated as sulphides.

No enrichment of Cd either in organic matter or in the fine sediment fraction was observed in the estuarine sediments. This points to the association of the metal with Fe and Mn oxyhydroxides. In a study by Morisson et al. (2001) also Cd did not correlate with organic carbon and Cauwet (1987) observed no enrichment of the metal in the fine sediments.

Seasonally, monsoon period was characterized by peak concentration and this can be related to the influx of metal-rich freshwater and increased land runoff characteristic of this season. The increased particulate matter along with suspended sediment load brought in by the rivers would also be a possible reason for the abnormally high Cd concentration. Lower concentration during summer may be due to the meagre runoff during this period.

Release of Cd from suspended particles and sediments has been reported in several estuaries (Salomons and Forstner, 1984; Ahlf, 1983; Calmano et al., 1985; Mart et al., 1985). Remobilization has been explained by complexing reactions with chloride and/or ligands from decomposing organic matter in water. In this way, uptake by suspended matter or precipitation onto it may be inhibited. Forstner
et al. (1989) suggested that significant amount of Cd is leached from surface sediments by the process of ‘oxidative pumping’. Since chloride complexes of Cd are very strong, during the premonsoon season, concentrations of these complexes are increased resulting in low metal concentration in sediments. Remobilisation of Cd in the postmonsoon season from surface sediments is possible as the particulate metal concentration was high during this season. Forstner et al. (1989) have further shown that salinity-influenced remobilisation was high for Cd. Hence, due to the increased complexation and remobilisation processes Cd concentration in the estuarine sediments are low in the non-monsoon periods.

**Lead**

Lead appears to be ubiquitous in the aquatic environment and generally does not bioaccumulate in aquatic organisms. Anthropogenic activities are responsible for most of the lead pollution (Scoullos, 1986). Combustion of oil and gasoline alone accounts for 50 percentage of all anthropogenic emission and thus constitute a major component in the global cycle of Pb. Pb accumulate in sediments (Zabel, 1989), therefore sediments serve as a Pb reservoir. Excess Pb, from water, as a result of contamination, may adsorb onto settling particulates and transport to sediments. In addition to adsorption, solid phase in which Pb may be present in sediments can regulate concentration of dissolved Pb. Because sediments play an important role in regulating Pb concentration in the interstitial waters and overlying waters, the investigation of its sediment content is necessary.

In this study, highest annual mean concentration was observed at one of the mangrove station closely followed by the riverine site. The highest concentration was recorded at Mangalavanam (station 1) where Pb concentration ranged from 17.99 to 94.11µg/g. At station 2, which is also a mangrove station, Pb varied from 22.71 to 52.17µg/g (Table A.57). However, at both these sites monsoon recorded the maximum concentration (Figure 5.27). In the river sediments, Pb varied from 14.18 to 86.41 µg/g and in the estuarine sediments, the variation was from 6.363 to 46.55 µg/g. Here also, monsoon season dominated in Pb content. ANOVA calculations also showed significant variation between stations (Table B.8).
Pb occurs only in divalent form Pb\(^{2+}\) in marine environments and hence it is not directly affected by fluctuating redox conditions. However, it can be influenced by secondary reactions such as sulphide concentrations. Significant drop in dissolved metal concentrations are observed when conditions changed from oxidized to highly reduced (Bragmann, 1988; Lu and Chen, 1977). Drysean (1985), by comparing the data on dissolved trace metals in anoxic waters pointed out the possible role of precipitating Fe(II) sulphides as a scavenger for other trace metals including Pb. Under anaerobic conditions FeS may be formed (Forstner and Wittman, 1979). Evans (1989) has also speculated on the co-precipitation of Pb with FeS. Fernex (1994) also opined that under anoxic condition, Pb could be bound to sediments as sulphides thus elevating the concentration. Intense anoxic conditions prevail in the mangroves due to the enormous load of organic matter in the system. Remineralization of this organic load wipes out all the oxygen that may be present in the system creating ideal condition for the metal to precipitate as sulphides. The very fine nature of mangrove sediments facilitates adsorption onto them and Pb bound in this way would remain unaffected by physical processes such as tides and currents.

Station 1 showed significantly higher values than station 2. At this station, Cd concentration was also very high. This points to a common source for these two metals presumably from leakages from petroleum storage place. Besides, Pb can have an atmospheric source through the emissions from automobiles. Since this site
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was located near the metropolis of Cochin, contamination from this source may be significant.

Seasonally, monsoon recorded maximum concentration of Pb. Pb, present in automobile fuels are identified as the single largest source of this metal to the atmosphere (Renner et al., 1998; Fernex, 1992). Pb, present in the atmospheric particulates is brought down by the heavy monsoon showers and they are rapidly settled to the sediments adding up the Pb pool of the system. In addition to this, increased land runoff of the season would also bring with it metal-rich particles eventually elevating the sediment Pb levels.

Among the hydrographical parameters, dissolved oxygen exhibited highly significant inverse relationship with the metal (Table C.3). This can be due to the increased precipitation of the metal as sulphides with decreasing dissolved oxygen levels. Highly significant correlation exhibited by Pb with Fe also augments this argument. As Forstner and Wittman (1979) have pointed out, under anoxic condition, FeS may form and Pb would have co-precipitated with FeS. Other than Fe, Pb was found to correlate with Zn, Cu and Co in the mangroves indicating their common fate in these sediments.

At both the stations, Pb was enriched in the finer sediments (table C.3). The increased specific surface area and the cation exchange capacity of the clay minerals both may have facilitated adsorption of the metal onto them. Many authors reported the affinity of Pb to clay minerals (Velde et al., 2003) in the mangroves. Organic matter did not appear to have any influence on metal concentration in the present study (Table C.12). In a study by Qu and Kelderman (2001), organic carbon showed negative correlation with Pb. Rosental et al. (1986) found no correlation between organic matter and Pb concentration in the sediments. The non-correlation indicates that there is different geochemical pathway for Pb other than diagenetic enrichment. Co-precipitation with FeS seems to be the main reaction mode for this metal in these highly anoxic systems.

In a previous study by Badarudeen (1997) Pb was reported in the range 11 to 49 ppm. Considering studies done elsewhere, the Brazilian mangrove sediments showed Pb in the range 1 to 8.9μg/g (Machado et al., 2002). However, Ong Che (1999) reported Pb in the range 72 to 195μg/g in the Mai Po mangroves, Hong Kong.
Pb exhibited high concentration in the sediments of the Chitrapuzha River. Here, Pb varied from 14.18 to 86.41 µg/g, with a monsoon maximum and a postmonsoon minimum. Pb was found to be enriched in the suspended particulate matter in the non-monsoon periods. Moore and Ramamoorthy (1992) have shown that in rivers, Pb was associated mainly with particulate matter. The increased particulate fraction of the metal may be the result of resuspension of sediments and the atmospheric fallouts. However, due to the increased runoff characteristic of the monsoon period would have facilitated leaching of metal-rich particles from the effluent discharge points and the leaching of atmospheric particulates.

The main contributor of Pb into this river may be effluent discharges. Nriagu (1979) has pointed out that environmental contamination of Pb arises from various sources such as manufacturing processes, paints and pigments, emission from motor vehicles, incineration of municipal solid wastes, combustion of coal and hazardous wastes. Effluent discharges from the various industries located near the sampling site may contribute Pb into this system. Anthropogenic Pb is mainly transported through the atmosphere (Martin et al., 1989; Guieu et al., 1991; Migon, 1993) and it is easily solubilized in water (Bethoux et al., 1990; Chester et al., 1990). In the water body, Pb divides into three — one part remains soluble, another becomes assimilated by plankton organisms and the third, bound to other trace metals, settles to the bottom.

Pb was found to be correlated well with organic matter in this river sediment. Moore and Ramamoorthy (1992) also observed that sorption of Pb by river sediments and correlation with organic content. Humic acids also sorb Pb and the process is found to be pH dependent. Positive correlation observed between Pb and pH (Table C.3) in this study reflects the association of Pb with humic substances, which forms a substantial portion of sedimentary organic matter. Many authors have speculated on the adsorption of Pb by sedimentary organic matter (Campbell and Evans, 1987; Seralathan, 1987; Nair and Ramachandran, 2002; Fan et al., 2001).

Pb showed significant correlation with other metals such as Mn, Zn and Cd at this site (Table C.10). Relatively high correlation with Mn suggests that Pb was trapped in the sediments during Mn precipitation. According to Fernex (1994), a trace metal like Pb$^{2+}$ can co-precipitate with a major dissolved metal like Mn$^{2-}$.
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during Mn oxide formation if this major ion is present in apparent over-saturation with respect to its oxides. Another possible way to enrichment of Pb with Mn in surficial sediments is due to the dissolution of Mn oxides in the deeper levels and ion migration to the upper levels where dissolved Mn precipitated. Adsorption of Pb on surfaces of oxides and hydroxides of Mn and Fe is well documented (Balistrieri and Murray, 1982, 1984; Scoullos, 1986). Balikangeri and Haerd (1988) have pointed out that with increasing pH, Pb (II) binds more strongly with MnO₄ surfaces. Krauskopf (1956) has stated that Pb is adsorbed consistently by hydrated Fe₂O₃ and MnO₂ is a good scavenger of trace elements in freshwater environments. Thus co-precipitation of the metal with Mn oxides seems to be the main mode of transfer of Pb in this river.

The estuarine sediments exhibited lower metal concentration than the river or mangrove sediments. Pb varied from 6.363 to 31.17 µg/g in the estuary. The general low values in the sediments can be related to the sandy nature of the substratum, which cannot hold metal ions effectively onto them. Another reason for the observed reduction in metal content at the estuarine mouth can be due to desorption of the metal that is concentrated in freshwater clay minerals. Partial removal of the element that is associated with oxides of Fe and Mn was also reported (Seralathan, 1987).

The main source of Pb into this estuary is presumably from anthropogenic activities. The rivers draining into this estuary carry with them effluents discharged from various industries. Since Pb is well known for aerial deposition, contribution from the Aeolian fallouts leads to elevated metal contents. Seasonally, monsoon season was characterized by the peak concentration. The heavy monsoon showers coupled with increased land run off contribute Pb-rich particles from atmosphere and effluent discharge points respectively to the estuary. Pb, in this study, did not exhibit any correlation with the hydrographical parameters reflecting its purely anthropogenic source (Table C.3). Other metals studied also showed no correlation with Pb in this estuary. Thus, Pb might have followed a different geochemical processing since it has a purely anthropogenic source. However, Pb was found to be enriched in the silt fraction of the sediment showing its preferential adsorption onto finer sediments.
5.5 Statistical Analysis

The assessment of pollution is based upon the determination of the concentration of the pollutants in the concerned environment. The enormous size of the data set usually present a problem in interpreting the results and in reaching a consistent conclusion. To avoid the errors that might have occurred during the analytical and/or sampling procedures, statistical analysis is necessary.

Correlation coefficients are indices that measure the strength of the linear relationship between variables. Emphasis is on the degree to which two sets of values vary together around their respective means and on the direction of co-variation of the variables.

If the sediment samples from the four different aquatic environments are considered as objects and the determined chemical parameters as variables, a correlation matrix can be obtained. This was studied in order to find the internal structure and assist in identification of pollutant sources not accessible at first glance. Since, in the present study, the calendar year was divided into three seasons with respect to monsoon, correlation study was carried out using seasonal data only.

Hydrographical parameters are the signature of aquatic systems. The four primary factors, salinity, dissolved oxygen levels, pH and temperature together determine the ultimate fate of a pollutant in the highly dynamic hydrosphere. Correlation study reveals the influence of each of them on the metal distribution. To understand the cumulative effect of these physico-chemical parameters, canonical regression analyses were carried out. In this, monthly data were adopted to evaluate the combined influence of these parameters by transforming them to a single linear function.

In all the systems analyzed, hydrographical parameters have an upper hand in determining the metal distribution as evidenced by their extremely significant regression coefficients (Tables D.1 to D.12). In all the three major fractions almost all metals correlated with the hydrographical parameters. Among the dissolved metals only Fe and Zn did not correlate well with physico chemical parameters at the reference station. This indicate the purely anthropogenic source of these metals.
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In the particulate fraction also Fe displayed non-correlation with hydrographical parameters at station 3 and at station 1, both Zn and Pb showed a similar behaviour. Besides Fe, Cu and Ni also exhibited less significant correlation with hydrographical parameters in the estuarine sediments. The non-correlation of Fe can be attributed to the relative abundance of the metal. Due to the enrichment of Fe in all the three phases, changes in the physico-chemical condition of the system have limited influence on the distribution of this element. Thus from the canonical regression analysis, it can be inferred that hydrographical parameters have an upper hand in regulating the trace metal chemistry in the mangrove, riverine and estuarine environments.

5.5.1 Principal component analysis

Due to the large number of variables and study locations, it was necessary to use some statistical technique to understand the results of the study. The multivariate analysis (principal component analysis or factor analysis) was adopted on the data matrix with columns representing the variables of a set and rows representing the observations. This approach helped to find the ‘latent’ variable that, in numbers smaller than the original ones, could explain the original variance and simultaneously reduce the dimensionality of the problem (Hopke, 1983; Wenchuan et al., 2001). By extracting the eigen values and eigen vectors of the matrix, the number of significant factors could be defined, the percentage of variance explained by each of them and the participation of the old variables in the new latent ones (Hopke, 1983; Pardo et al., 1990). The explained variance of some factors can be defined as the percentage of sum of the variance of these factors as a function of the total variance. Factors with eigen values greater than one were selected (Davis et al., 1973).

Trivial factors were eliminated by normalizing during rotation factor loadings by the Varimax method (Borovec, 1996). In this way, two factors were accounted in this study and the remaining factors did not give significant contribution to the information included in the data matrix. The composition of the first two principal components was referred to as ‘principal component loadings’ is reported in the table.
By using the multivariate methods, the dimensionality of the problem was reduced from the original 120 chemical variables to only two key factors. These variables are built by means of a linear combination of the original ones and the eigen vectors and can be plotted to obtain a graphical picture of the overall situation. The principal component score plot was used to interpret the spatial distribution by clustering the samples. It was also used to describe their different characteristics and help to find out the sources of heavy metal in the surficial sediments. Only sediment samples were selected for this analysis as they record pollution for considerably longer times.

<table>
<thead>
<tr>
<th></th>
<th>Factor 1</th>
<th>Factor 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.7077</td>
<td>0.5733</td>
</tr>
<tr>
<td>Mn</td>
<td>0.9354</td>
<td>0.0849</td>
</tr>
<tr>
<td>Zn</td>
<td>0.7254</td>
<td>0.6252</td>
</tr>
<tr>
<td>Cu</td>
<td>0.6203</td>
<td>0.7517</td>
</tr>
<tr>
<td>Co</td>
<td>0.6229</td>
<td>0.7369</td>
</tr>
<tr>
<td>Cr</td>
<td>0.1677</td>
<td>0.7643</td>
</tr>
<tr>
<td>Ni</td>
<td>0.5921</td>
<td>0.7879</td>
</tr>
<tr>
<td>Cd</td>
<td>0.9284</td>
<td>0.0586</td>
</tr>
<tr>
<td>Pb</td>
<td>0.6336</td>
<td>0.7078</td>
</tr>
<tr>
<td>Org. C</td>
<td>-0.1336</td>
<td>0.8888</td>
</tr>
<tr>
<td>Expl. Var</td>
<td>4.3346</td>
<td>4.3340</td>
</tr>
<tr>
<td>Prp. Totl</td>
<td>0.4335</td>
<td>0.4334</td>
</tr>
</tbody>
</table>

Table 5.28: Factor loadings of metals at station 1

<table>
<thead>
<tr>
<th></th>
<th>Factor 1</th>
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</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.9028</td>
<td>0.1264</td>
</tr>
<tr>
<td>Mn</td>
<td>0.7955</td>
<td>-0.1248</td>
</tr>
<tr>
<td>Zn</td>
<td>0.8882</td>
<td>0.4015</td>
</tr>
<tr>
<td>Cu</td>
<td>0.6244</td>
<td>0.7103</td>
</tr>
<tr>
<td>Co</td>
<td>0.8633</td>
<td>0.3090</td>
</tr>
<tr>
<td>Cr</td>
<td>0.6500</td>
<td>0.2124</td>
</tr>
<tr>
<td>Ni</td>
<td>0.8353</td>
<td>0.4780</td>
</tr>
<tr>
<td>Cd</td>
<td>0.7149</td>
<td>0.4687</td>
</tr>
<tr>
<td>Pb</td>
<td>0.9356</td>
<td>-0.0325</td>
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<tr>
<td>Org. C</td>
<td>-0.0794</td>
<td>0.9140</td>
</tr>
<tr>
<td>Expl. Var</td>
<td>5.8847</td>
<td>2.1224</td>
</tr>
<tr>
<td>Prp. Totl</td>
<td>0.5885</td>
<td>0.2122</td>
</tr>
</tbody>
</table>

Table 5.29: Factor loadings of metals at station 2

At station 1, the first factor showed positive loading with Fe, Mn, Zn and Cd (Table 5.28). The order of significant loading were Mn > Cd > Zn > Fe. The second factor showed positive loading with organic C, Ni, Cr, Cu and Co. Hence, at this site Cd and Zn were mainly associated with Fe and Mn oxides while, the rest were associated with organic matter. The principal component score plot distinctly showed two groups of elements. Cd and Mn formed one group, while Fe and Zn, Ni, Cu, Co and Pb formed another cluster (Figure E.1). Thus, from this score plot,
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it is very clear that Cd was present mainly associated with Mn oxides rather than Fe oxides whereas for Zn, the reverse seems to be true. Cr and organic carbon were separated from the rest in the mangroves. Enormous load of organic matter degraded in the mangroves may have led to the abundance of large organic molecules, leaving limited chances of complexation with the metals. However, due to the natural affinity of the metal cations to the negatively charged organic coatings, in turn, leads to the observed positive loading of some metals with this variable. At station 2 also, organic C was found to have a positive loading with Cu (Table 5.29). Rest of the metal was concentrated in the first factor. At this site too, organic C was separated from the rest in the factor score plot (Figure E.2).

<table>
<thead>
<tr>
<th></th>
<th>Factor 1</th>
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</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.9582</td>
<td>0.0243</td>
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<tr>
<td>Mn</td>
<td>0.1086</td>
<td>0.9334</td>
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<tr>
<td>Zn</td>
<td>0.3210</td>
<td>0.9244</td>
</tr>
<tr>
<td>Cu</td>
<td>0.8498</td>
<td>0.4850</td>
</tr>
<tr>
<td>Co</td>
<td>0.7378</td>
<td>0.5762</td>
</tr>
<tr>
<td>Cr</td>
<td>0.2918</td>
<td>0.5267</td>
</tr>
<tr>
<td>Ni</td>
<td>0.8687</td>
<td>0.4591</td>
</tr>
<tr>
<td>Cd</td>
<td>0.5979</td>
<td>0.6454</td>
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<td>Pb</td>
<td>0.6128</td>
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<td>Org. C</td>
<td>0.7124</td>
<td>0.3771</td>
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<tr>
<td>Expl.Var</td>
<td>4.3799</td>
<td>3.8970</td>
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<tr>
<td>Prp.Totl</td>
<td>0.4380</td>
<td>0.3897</td>
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</tbody>
</table>

Table 5.30: Factor loadings of metals at station 3

<table>
<thead>
<tr>
<th></th>
<th>Factor 1</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0.8368</td>
<td>0.4742</td>
</tr>
<tr>
<td>Mn</td>
<td>0.2464</td>
<td>0.8884</td>
</tr>
<tr>
<td>Zn</td>
<td>0.7389</td>
<td>-0.0728</td>
</tr>
<tr>
<td>Cu</td>
<td>0.8424</td>
<td>0.4293</td>
</tr>
<tr>
<td>Co</td>
<td>0.6890</td>
<td>0.5716</td>
</tr>
<tr>
<td>Cr</td>
<td>0.7676</td>
<td>-0.0132</td>
</tr>
<tr>
<td>Ni</td>
<td>0.8840</td>
<td>0.4105</td>
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<tr>
<td>Cd</td>
<td>-0.2740</td>
<td>0.8303</td>
</tr>
<tr>
<td>Pb</td>
<td>0.2525</td>
<td>0.2532</td>
</tr>
<tr>
<td>Org. C</td>
<td>0.8618</td>
<td>-0.0438</td>
</tr>
<tr>
<td>Expl.Var</td>
<td>4.7436</td>
<td>2.4546</td>
</tr>
<tr>
<td>Prp.Totl</td>
<td>0.4744</td>
<td>0.2455</td>
</tr>
</tbody>
</table>

Table 5.31: Factor loadings of metals at station R

However, at the riverine site, factor 1 displayed positive loading with Fe, Cu, Co, Ni and organic matter (Table 5.30). Here, Mn was found to positively loaded with Zn and Pb. Hence, it can be inferred that Cu, Co and Ni were adsorbed either onto Fe oxides or organic matter, while Mn seems to be primary carrying phase for Zn and to a lesser extent, Pb. Another combination of metals was seen at the estuary. Here, Fe, Zn, Cu, Cr, Ni and organic matter showed positive loading with factor 1, while, Mn and Cd were loaded with factor 2 (Table 5.31). Score plots of
factors showed a combination of Fe, Cu, Co and Ni and another group of Zn, Cr and organic matter (Figure E.4). Association of Zn and Cr in these estuarine sediments points to their common source in these estuarine sediments, presumably from the leakage from boats.

5.5.2 Cluster analysis

A simple model was obtained for the relationship amongst the test elements by cluster analysis, based on the weighted pair-group method with arithmetic averages. The single linkage method was used. The most similar sites are grouped together. The resultant dendrograms depict the sequence in the associations of sites, similar to the correlation matrix, but in a more lucid form. Trace metals in all the three phases were put together to get the dendrogram by the 'joining tree' diagram. This analysis revealed that the estuarine as well as station 1 were the most similar in the processes that determine the fate of trace metals in these aquatic systems. The other mangrove station (station 2) behaved differently, since the physicochemical environment was severely influenced by human interferences. The riverine site, exhibited dissimilar hydrogeochemical processes.

Figure 5.28:- Dendrogram of trace metals
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