CHAPTER 6
TRACE METALS

The term ‘heavy metal’ refers to all metals and metalloids with the exception of alkali and alkaline earth elements, having a density five times higher than that of water, specific heat above four or five and atomic weight more than twenty. They are generally termed ‘trace metals’ or ‘trace elements’ in current literature to designate the elements which occur in trace amounts (few parts per million) in natural biological systems. Thus for practical purposes, the terms such as ‘heavy metals’, ‘trace inorganics’ and ‘micronutrients’ are treated as synonymous with the term trace elements (Wittmann, 1979).

Trace metals play a dual role in living systems. Many of these metals known as ‘essential elements’ are crucial for the sustenance of life, although only in very small quantities. An element is essential when (i) it is consistently determined to be present in all healthy living tissues within a zoological family, whereby tissue concentrations from species to species should not vary by a wide range (ii) deficiency symptoms are noted with depletion or removal and disappear when the elements are returned to the tissue and (iii) the deficiency symptoms should be attributed to a distinct biochemical defect on the molecular level (Overhoff and Forth, 1978). Metals are not identifiable as serving as beneficial biological functions are referred to as nonessential.
Uptake of most of these elements beyond certain critical limits results in toxic reactions (Purves, 1985). The differences between the nutritive function and toxicity are only a matter of variation in concentrations of metals in the organisms and generally the differences are large enough to cause any practical concern (Byrne and Miller 1984; Waldichuk, 1985).

Trace metals may accumulate unnoticed to toxic levels. Virtually all the metals can produce toxicity when ingested in sufficient quantities, but these are pervasive or produce toxicity at all concentrations. In general, trace metals produce toxicity by forming complexes with ligands of organic compounds. Most common groups involved in ligand formation are oxygen, sulphur and nitrogen when metals bind to these groups, they may inactivate important enzyme systems or affect protein structure. Hence the problems related with heavy metal contamination were first highlighted in the industrially advanced countries because of their large industrial discharges and especially by incidents of mercury (Minamata disease) and Cadmium (itai-itai) pollution in Japan and Swedan (Kurland et al., 1960; Irukayama et al., 1961; Gold water, 1971; Nitta, 1972; Hagino and Yoshioka, 1961; Kogai, 1975; Goldberg, 1976). Trace metals are continuously released into the biosphere through processes like volcanisation, geological weathering of rocks, urbanization, industrialization, agricultural run off, mining activities, anthropogenic activities, smelting, burning and combustion of fossil fuels etc.

The importance of estuaries lies in the fact that they act as a mediator/filter in the transfer of elements from continents to oceans. During estuarine mixing, a very large proportion of metals in dissolved complex species undergoes flocculation from the particulate matter and tend to be adsorbed onto suspended particles or bound to oxides, hydroxides, phosphates, sulphates, carbonates and organic matter (Thangaduri et al., 2005) and are
scavenged from the water column into proximal sediment (Santchi et al., 1990). These sediments become an important reservoir for metals and provide a good index to assess the pollution load, trace the source and the routes of movement (Salamons and Forstner, 1984; Zwolsman et al., 1999).

Mangrove sediments act either as sources or as sink for trace metals as in other coastal marshes (Lacreda et al., 1987; George Thomas and Fernandez; 1997a). Salt marshes, particularly those located near or along estuaries such as mangrove forests are often polluted by river borne and marine derived particles and pollutants (Tam and Wong, 1995). Mangroves play an important role in the abatement of metal pollution. Trace metals enter into mangroves with incoming tide associated with suspended particles and oxy-hydroxides of metals. When these entities meet with the reducing condition, dominant in mangroves, these oxy-hydroxides are reduced, dissolve and release their trace metal load into the water column. Due to the permanent anoxic condition of mangrove sediments and high sedimentation rates, trace metals suffer rapid accumulation and buried in the sediment column. Thus mangroves can act as biogeochemical barriers to the transport of trace metals to coastal waters. Clay minerals and organic matter are important carriers of trace metals in sediment (Brook and Moore, 1988).

Sediment parameters such as grain size, pH, organic carbon content and total phosphorus can profoundly influence the distribution of trace metals and microorganisms in sediments (Fukami et al., 1993). Trace metals are non-degradable pollutants which create an environmental stress and often magnified in the food chain through the different trophic levels causing a deleterious effect on the living organisms (Nitta, 1992). Metals are natural constituents of aquatic body and the analysis and evaluation may help assessing the inputs resulting
from human activities, the erosion of ore bearing rocks, volcanic activity, forest fire and vegetation (Deepak and Sahu, 1999).

A number of studies have addressed the influence of hydrographic parameters viz., pH, DO, turbidity and salinity on the chemistry of trace metals under estuarine conditions (Sholkovitz, 1976, 1978; Santschi et al., 1980; Bourg, 1983; Windom et al., 1983; Millward and Turner, 1995). The distribution pattern of Cu, Ni, Fe, Co, Ti and Mn in the sediments of Vembanad Lake has been extensively studied by Murty and Veerayya (1981). Variation of Cu, Pb and Cd in the estuarine sediments under the marine influence was reported by Forstner et al. (1990) for Elba estuary. Chakrapani and Subramanian (1990) and Ramesh et al. (1990) observed that trace metal concentrations varied considerably with the basin and he attributed this variation, in part, to human influence. Konhauser et al. (1997) found that high proportion of trace metal content resided in the clay material less than 2μm. Several authors carried out investigations to assess the trace metal content of the Cochin estuary (Murty and Veerayya, 1981; Venugopal et al., 1982; Paul and Pillai, 1983; Ouseph, 1987; Nair et al., 1990; Resmi, 2004). Trace metal concentration in Ashtamudi estuary has been studied by Geetha Bhadran (1997); that in Poovar estuary by Nejmi (2000), Pumba River by Mathew Koshy (2001) and in Karamana River by Padmalal (1992) and Jayaraman (2003). Several investigators repeatedly advocated that metal scavenging ability of sediments increase as the particle size decreases (Gibbs, 1973; Nair and Balachand, 1993; Panigrahy et al., 1999; Unnikrishnan, 2000).

Trace metals affect the activity of microbes and influence the abundance and diversity of organisms. The biological effect of these metals have demonstrated that even very low concentration of it can inhibit photosynthesis
or growth of many species of bacteria (Albright et al., 1972; Gonye and Jones, 1973).

From a biological perspective, metals may be classified into those that are essential to living organisms, those that are potentially toxic but which, due to their general rarity in the environment, are relatively unavailable. At least eleven of them are essential for growth and various life activities of organisms, including man (Kawser Ahmed et al., 2002). They include Cu, Zn, Co, Ni, Fe, Mn, Mo, Se and Ti (Dasilva, 1978). These elements are vital components of proteanaceous enzymes (Zn); respiratory pigments (haemoglobin in man-Fe and haemocyanin in mollusc-Cu) and certain nutritional elements (Vit B12-Co) of organisms. Certain trace metals gained importance for their active participation in metabolic reactions as well as their inhibitory role in the nutrient utilization by plants (Khan and Khan, 1983). Some of them get biomagnified in the water and get accumulated in fish, crabs and other aquatic organisms (Trivedi and Goel, 1986). Other trace metals viz., Pb, Cd and Hg are considered as non-essential, because they have no known biological role, these become highly toxic when found at metabolically active sites, even at relatively low concentrations. These elements get magnified in food chains and reach human beings causing deleterious effect. Such toxic metals may cause serious abnormalities in living organisms (Pandit and Padmakumar, 1999; Samantha, 2000) and their environment (Griffin and Juninak, 1973; Rajan and Witkinson, 1976; Chen and Wu, 1995; Perin et al., 1997; Riedel et al., 2000). Hence information on the level of trace metals in aquatic environment is significant in many respects.

All metals essential to life are toxic when supplies in excess of the optimum concentration levels. For e.g. essential trace metals such as Zn becomes toxic when the nutritional supply becomes excessive. A metal in trace
amounts i.e. smaller than 0.01% of the mass of the organism is essential when an organism fails to grow or complete its life cycle in the absence of that metal. However the same metal is toxic when concentration levels exceed those required for correct nutritional response by factors varying between 40 and 200 fold (Venugopal and Luckey, 1975). Deficiency, excess beyond threshold and limiting value of trace metals give rise to detrimental effects. Cd and Pb are highly toxic heavy metal and cause many serious abnormalities in living organisms and their environment (Pandit and Padmakumar, 1999).

Monitoring of trace metal concentration in sediments is an integral part of any environmental management programme such as mineral exploration (Hawkes and Webb, 1962; Forstner and Wittmann, 1979; WHO, 1982; Hakannson and Jansson, 1983; Sinex and Wright, 1988; Hoshika et al., 1991), geochemical flux calculations (Burton, 1978; Martin and Maybeck, 1979; Salomons and Forstner, 1984; Seidemann, 1991) and determination of effectiveness of pollution control programmes (Salomons and Eysink, 1981).

The distribution of trace metals in sediments is an important area of research in environmental studies. Sediments not only reflect the current quality of water, but also provide vital information on the transportation and fate of pollutants (Finney and Huy, 1989; Santschi et al., 1990). The significance of studies of metal distribution among various geochemical phases of sediment in determining the potential bio-availability and remobilization of trace metals has been emphasized also by Forstner et al. (1990) and Izquierdo et al. (1997). Thus it is necessary to identify and quantify the metal forms in order to assess the environmental impacts of contaminated sediments.

Environmental contamination is an inevitable consequence of human activity. The sediments deposited in estuarine and coastal environments are
becoming increasingly polluted with minor metals due to urban and industrial development in coastal areas (Thangaduri et al., 2005). Hence, understanding the source of pollution in offshore aquatic systems is important to monitor environmental degradation.

Trace metal contamination in sediments is one of the great concerns to environmental quality and human health. The distribution of trace metals in sediments is thus a prime area of research in environment studies. Hence the present analysis encompasses an assessment of the spatial and temporal variations in the distribution of trace metals viz., Cu, Zn, Pb and Cd in the sedimentary environments of mangrove and non-mangrove sites of Ashtamudi lake and the factors controlling their source, fate and dynamics and related ecotoxicological implications with a view to asses the degree of contamination in the estuarine system.

The geochemical data of the sediment in the Ashtamudi Lake was evaluated to assess the degree of contamination. (Forstner and Wittman, 1979; Brook and Moore, 1988; Nair et al., 1990; Rajendran, et al., 1996; Paucot and Wollast, 1997; and Hatje et al., 2001). Further, an attempt has also been made to compare the results obtained in the present investigation with world averages (average shale and earth’s crust-Turekian and Wedepohl, 1961, Taylor, 1964), various local, Indian and foreign rivers, estuaries and sediments (Table 6.1.).

6.1. Copper

Copper (At. No. – 29, At. Wt. 63.55) is the most common metal essential for all biological life, but is toxic at higher concentration especially in the early developmental stage of many organisms (Spear and Pierce, 1979). It is required in catalytic amounts to carry on various enzymatic reactions in the
cells, as a cofactor. The presence of copper in plant and animal tissue was realized / recognized more than 150 years ago and it was shown to exist in combination with the blood protein in snails. The first indication of copper deficiency occurs naturally in livestock dates back to 1931 with regard to ‘salt-sick’ cattle in Florida. The excessive intake of Cu (> 470mg) in human body is toxic, which results, in its accumulation in the liver, causes hypertension, sporadic fever, coma and even death. Copper also produces pathological changes in brain tissue (Kudesia, 1990). Cu in aqueous systems received attention mostly because of its toxic effect on biota.

Copper reaches the aquatic environment directly from copper mines and a large number of industrial processes like agricultural chemicals, paints etc. Sewages, industrial effluents and electric generating plants also contain this metal. Copper occurs in many organic and inorganic forms in the aquatic environment. After entry into the aquatic system, copper may remain dissolved or adsorbed by organisms. Sediments are regarded as an important sink for the removal of copper. Excess of copper from the water may get adsorbed onto particulate and settle to bottom sediments. If water is depleted of the metal, the adsorbed copper may re-dissolve or desorbs to increase its concentration in the interstitial waters. Thus sediments are involved in determining the fate of copper in the aquatic environment.

Copper concentration ranges from 2 to 100 ppm in soil, while its concentration is between 0.0006 to 0.4 ppm in unpolluted water. Sediments free from industrial and sewage pollution ranges from 0.5 to 16.8 ppm. 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). The reactivity will depend on both the chemical and physical environment to which copper is introduced. The free
copper ion interacts with the organic matter present but the result is usually an increase in solubility, rather than sedimentation (Nelson and Lund, 1982; Windom et al., 1983).

The behavior of copper in rivers was predicted to be similar to that of zinc, based on the Malti river associations summarized by Martin and Meybeck (1979). They suggested that 10 to 50 percentage of total copper would be in the dissolved phase. The strong tendency of copper to remain in solution from the decay of vegetative matter may stabilize copper. Fresh water contained 69 % copper in dissolved fraction, while it was reduced to 21 % in estuarine water. Feely et al. (1982) showed that the sewage effluent receiving stations had very high amounts of trace metals in organic bound form. Tessier et al. (1980) also observed high percentage of total copper bound to organic matter for the particulate matter of Yamaska and St. Francisco rivers. This result was partly explained by the fact that for most ligands copper exhibited the highest stability constants of all the metals considered (Smith and Martell, 1976; Stumm and Morgan 1981; Samanidou and Fytianos, 1987; Pardo et al; 1990). Shibu et al. (1990) observed that the copper in the estuarine and fresh waters of Cochin estuary was extensively associated with organic matter. Flemming and Trevors (1989) reviewed that available scientific literature on copper toxicity and chemistry of the environment and concluded that the chemical form of copper was important in controlling its geochemical and biological behaviour. Baker (1990) summarized the chemistry of copper in soils and pointed out that the plant availability depended on a number of soil factors which controlled its chemical speciation. copper forms sulphides, sulphates, carbonates and other compounds under natural conditions while this metal is also associated with organic matter, oxides of iron and manganese, silicate clays and other minerals.
The seasonal distribution of copper in the sediments of Ashtamudi Lake is depicted in Fig. 6.1. and the monthly data in Appendix Table 6.1. The monthly distribution of copper ranged from 1.20 µg g⁻¹ (December) to 22.00 µg g⁻¹ (May) at Station 1, 2.40 µg g⁻¹ (August) to 32.40 µg g⁻¹ (May) at Station 2, 3.80 µg g⁻¹ (April) to 52.00 µg g⁻¹ (September) at Station 3, ND (September, October and December) to 46.00 µg g⁻¹ (May) at Station 4, 1.40 µg g⁻¹ (December) to 13.80 µg g⁻¹ (May) at Station 5, 22.40 µg g⁻¹ (April) to 37.40 µg g⁻¹ (November) at Station 6 and 2.60 µg g⁻¹ (December) to 18.00 µg g⁻¹ (April) at Station 7. Highest concentration was observed at Station 3 (52.00 µg g⁻¹) in the month of September, while the lowest (1.20 µg g⁻¹) at Station 1 during December.

Seasonally, the copper content in the sediment fluctuated between 7.28 and 41.78 µg g⁻¹; 3.75 and 36.15 µg g⁻¹ and 9.70 and 30.60 µg g⁻¹ during monsoon, postmonsoon and premonsoon periods respectively. Copper was found below detectable level at Station 4 in the month of September, October and December. The highest amount of copper observed at Station 3 during monsoon may be due to the use of CuSO₄ as fungicide in agricultural fields as a result of influx of fresh water from the Kallada River. The highest value of copper observed at Station 3 during post and premonsoon may be due to the settling of copper after monsoon. The highest value of copper was recorded at Station 3 followed by Station 6 and 7 where the anthropogenic activities are higher. In general, copper in the sediments was released into the dissolved phase as it entered saline water region from the fresh water regions. Salomons and Bril (1990) demonstrated the copper contamination in the sediments of Fly River in Papua New Guinea. Salmons and Eagle (1990) confirmed the release of copper in Fly River sediments, from their field studies. On an annual basis, the maximum copper content was observed at Station 3 followed by Station 6. Copper is always found to be strongly complexed in estuarine and
marine waters (Voelkar and Kogut, 2001). Copper at Station 3 exhibit premonsoon > postmonsoon > monsoon trend. The decrease in copper content at Station 4 may be due to marine influence. Significant month wise and station-wise variations were noticed in sedimentary copper as revealed by ANOVA: (monthwise - $F = 2.6057; d.f. = 11; p \leq 0.008$; Stationwise - $F = 27.5345; d.f. = 6; p \leq 3.3551E-16$) however, no significant seasonwise variation were evident.

Among the two biomes analyzed i.e., mangrove and non-mangrove/estuary; mangrove was found to have comparatively higher sediment copper content than the estuary. Seasonal distribution was different for the two biomes. Monsoon season was characterized by peak concentration at Station 3 and with a minimum during postmonsoon period at Station 1. However, distinct seasonal variation was difficult to observe at non-mangrove stations 4 and 7. Slightly higher values were observed at Station 4 and 7 during the premonsoon period.

Forstner et al. (1989) observed that copper to be present in large quantities in sediments in the anoxic condition than in oxic condition. They further showed that copper complexation with organic matter has a dominant role in the transfer of the metal to biologically inactive form. Sulphides of copper are found to be more stable in the anoxic sediments (Westerlund et al., 1986). Tam and Wong (1996) showed that sulphide precipitation is very important in mangrove sediments. Low redox potential in the mangrove sediments indicates the presence of significant quantities of $\text{H}_2\text{S}$ that precipitates metals in insoluble sulphide forms (Huerta-Diaz and Morse, 1992). Hence the elevated copper concentration in the mangrove sediments may be due to the increased precipitation of the metal as insoluble sulphides. Heraldson and Westerlund (1988) also observed a rapid decrease in dissolved copper in the anoxic zones of the Black Sea and Frum Varren Fjord, Norway.
The concentrations of sedimentary copper noticed in this study were much lower than those reported earlier. Badarudeen (1997) reported copper in the range 15 - 91 ppm in Cochin mangroves. Copper concentration ranged from 18 - 80 µg g\(^{-1}\) in the Brazilian mangroves whereas 51-87 µg g\(^{-1}\) in the Mai Po mangroves, Hong Kong (Machado et al., 2002). Seralathan (1987) recorded concentration of copper ranged from 70 to 78 µg g\(^{-1}\) in Cauvery mangroves.

In the present analysis of sedimentary copper, the monsoon period was characterized by the highest concentration while the minimum was recorded during the postmonsoon season. Since the maximum concentration was observed in the rainy season, the main source of copper in this aquatic system may be the high run off. The heavy influx of freshwater might have leached the metal-rich particle from the effluent discharge points elevating the metal load in the monsoon season. Biksham et al. (1991) found enrichment of copper in the suspended sediments of the Godavary River, India.

The estuarine sediments showed remarkably low copper concentration. Maximum concentration was recorded during premonsoon while the minimum was observed during postmonsoon period. 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. In a study by Helland (2001) in a micro tidal estuary, only a small amount of copper was associated with particles and settled out. Relatively high concentration of copper was observed in the sediments of Thannirbavi River, Mangalore, from the vicinity of effluent discharge point of a chemical and fertilizer factory (Krishnakumar et al., 1998). This finding again confirms the reductive dissolution of copper from the sediments. Relatively high concentration of the element in the mangrove may be due to its release from organisms during their decomposition. Thus, the enhanced level of copper during premonsoon season...
observed in this study may 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. The intense boat traffic in the estuary may also have contributed considerable amounts of copper to the estuarine sediments. Mohan (1997) observed higher copper content in the Vellar River than the estuary and related this to high amount of fine sized particles.

The mean sedimentary copper content in the Ashtamudi lake was found to be lower as compared to standard values of average shale, earth’s crust, average Indian river sediment and aquatic systems viz., the Vellar estuary, Poovar aquatic system, River Pumba, River Ganga, Brahmaputra, Godavari, Krishna, Narmada, Tapti, Cauveri, Vamsadhara, Pisuerga (Spain), Kaohshiung (Taiwan) and Scheldt (France). The values were higher than that of the Yarra river estuary (Astralia), the Cochin backwaters, the Subarnarekha river and the Vellar river. Sedimentary copper concentration lower than that of the present study was reported in the Cauveri River (12.00 µg g⁻¹) by Subramanian et al. (1985). In River Ganga, Samantha (2000) and in Karamana river, Jayaraman (2003) recorded sedimentary copper content more or less comparable to that of the present study and mean value of copper content in the present study agreed with that of the Bharathapuzha, a less polluted river in Kerala (Table6.1.)

Sedimentary copper showed significant positive correlation with sedimentary Zn (Cu vs Zn - r = 0.8076, y = 28.3927 + 1.57601x, p ≤ 1.68E-20, n = 84), and Pb (Cu vs Pb - r = 0.2173, y = 114.6511 + 0.8545x, p ≤ 0.05, n = 84), while Cd showed no relationship with Cu, besides Cu exhibited significant positive correlation with fine grained sedimentary fractions (Cu vs Silt + Clay - r = 07678, y = 16.9083 + 1.2509x, p ≤ 1.58E-17, n = 84), SOC (Cu vs SOC-r = 0.6812 y = 6.1672 + 0.0976x, p ≤ 2.84E-10, n = 84), Sedimentary carbohydrate (Cu vs CHO - r = 0.6214 y = 1.7845 + 0.3748x,
Fig. 6.1 Seasonal distribution of Copper μg g⁻¹

![Copper distribution graph]

Fig. 6.2 Seasonal distribution of Lead μg g⁻¹

![Lead distribution graph]
6.2. Lead

Lead (At. no. - 82 At. wt. - 207.2) is a non-essential metal (Dasilva, 1978), but it is present in all tissues and organs of animals. Lead resembles the divalent alkaline earth group metals in chemical behaviour. Metabolism of lead is similar both in their deposition in and mobilization from bone. Under normal conditions, more than 90% of the lead retained in the body is in the skeleton. It inhibits the biosynthesis of haem and thereby affects membrane permeability of kidney, liver and brain cells. The toxicity of lead has been known to mankind for many centuries. The great poet-physician Nicader over 200 years ago described the disease known as Plumbism, which is caused by acute lead poisoning. Childhood lead poisoning is a real problem in many of the urban areas, especially slums, and is a major source of brain damage, mental deficiency and serious behavioral problems. Yet, Plumbism is an insidious disease and difficult to diagnose. One of the most common consequences of long term lead poisoning is chronic kidney infection known as nephrites.

Lead appears to be ubiquitous in the aquatic environment and generally does not bio-accumulate in aquatic organisms. Anthropogenic activities are
responsible for most of the lead pollution (Scoullos, 1986). Lead accumulates in sediments and hence sediments serve as a lead reservoir (Zabel, 1989). 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 complexation with organic or inorganic ligands. The degree of mobility of lead depends on the physicochemical state of the complexes formed.

Concentration of lead in uncontaminated fresh water is generally $\leq 3 \mu g \ l^{-1}$. However, much high levels often occur near the high ways and urban regions due to the combustion of gasoline. Pande and Das (1980) reported that rivers at the major industrial zones may contain up to 20-89 $\mu g \ l^{-1}$ of lead.

Trace metals are added to the estuary mainly via riverine input, weathering and remobilization from sediments (Chester, 1986; Jickells et al., 1987). For metals such as lead that bind strongly to particle surface and have no biological functions, the dominant removal process is by adsorption onto particulate materials, which then, sinks and transports the metal to the bottom (Fowler and Knaver, 1986). Lead content in the aquatic systems can be recognized into three components—one part remaining soluble, another getting assimilated by plankton organisms and the third, remaining bound to other trace metals, and finally settling to the bottom.

The monthly distribution of lead in the sediments of Ashtamudi Lake is depicted in Appendix Table 6.2. and the seasonal distribution Fig. 6.2. The monthly distribution of lead in the sediments varied from 6.00 $\mu g \ g^{-1}$ (November) to 240.00 $\mu g \ g^{-1}$ (January) at Station 1, 28.00 $\mu g \ g^{-1}$ (October) to 216.00 $\mu g \ g^{-1}$ (September) at Station 2, 58 $\mu g \ g^{-1}$ (October) to 244.00 $\mu g \ g^{-1}$ (December) at Station 3, 52.00 $\mu g \ g^{-1}$ (December) to 164.00 $\mu g \ g^{-1}$ (January) at Station 4, 30.00 $\mu g \ g^{-1}$ (June) to 220.00 $\mu g \ g^{-1}$ (March) at Station 5,
28.00 µg g⁻¹ (September) to 200.00 µg g⁻¹ (May) at Station 6, and 22.00 µg g⁻¹ (August) to 154.00 µg g⁻¹ (February) at Station 7. The seasonal values of lead fluctuated between 76.00 to 162.50 µg g⁻¹, 94.00 to 162.50 µg g⁻¹, and 110.50 to 176.50 µg g⁻¹ during monsoon, postmonsoon and premonsoon seasons respectively. In this study, the highest annual mean concentration was observed at the mangrove sites viz., Station 3 (159.70 µg g⁻¹) followed by the Station 1 (144.50 µg g⁻¹).

Badarudeen (1997) reported lead concentration ranging between 11.00 and 49.00 µg g⁻¹ in Cochin mangrove. The Brazilian mangrove sediments showed lead content that ranged from 1.00 to 8.90 µg g⁻¹ (Machado et al., 2002). However, higher lead content in the range of 72.00 to 195.00 µg g⁻¹ was reported in the sediments of Mai Po mangroves, Hong Kong by Ong Che (1999).

Seasonally, maximum concentration of lead was recorded during premonsoon. Lead present in automobile fuels is identified as the single largest source of this metal to the atmosphere (Renner et al., 1998; Fernex et al., 1992). Lead, present in the atmospheric particulates is brought down by the heavy monsoon showers and they are rapidly settled to the sediments adding up the lead of the system. In addition to this, increased land run off of the season would also bring with it metal rich particles eventually elevating the sedimentary lead levels. The monsoon hike of sedimentary lead observed as a consequence of the above phenomenon corroborates with the earlier findings of Ouseph (1992) and Joseph (2001). Maximum concentration of lead was exhibited at Stations 3 and 1 during monsoon and postmonsoon respectively. Comparatively higher concentration observed at this site might have resulted from river discharge into the estuary as reported elsewhere (Boyle et al., 1974; Sholkovitz, 1976; Danielsson et al., 1983; Windom et al., 1983, 1988; Ouseph, 1992;
Riso et al., 1993; Cotte-Krief et al., 2000; Saad et al., 2003). The phases of variation observed herein depending on the sampling stations indicated the complex factors controlling the seasonal variations of this metal. Nair et al. (1987) reported the lead content ranging from 67.00 to 92.00 μg g⁻¹ in the Ashtamudi estuary while Geetha Bhadran (1997) registered a lower value of 8.50 to 34.75 μg g⁻¹ in the same aquatic system. However, in the present investigation, values remained higher (76.00 to 176.50 μg g⁻¹) may be under the influence of anthropogenic inputs including enhanced vehicular transport.

No significant spatial and temporal variations were noticed in the distribution of sedimentary lead. The maximum concentration of lead in this study observed at Station 3 (244.00 μg g⁻¹) and Station 1 (240.00 μg g⁻¹) during postmonsoon season. The minimum was observed at Station 1 (6.00 μg g⁻¹) also during postmonsoon. The sedimentary lead content at various stations was found to be in the increasing order of - Station 4, 7, 2, 5, 6, 1, 3. Highest concentration of lead was exhibited in the mangrove sites during all the seasons. The elevated metal level recorded herein may be ascribed to the anthropogenic inputs along with the high land run off. Besides, a benthic flux of lead is also expected at this site as opined by 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 fractions with relatively high levels of organic matter (Aller and Beniger, 1981; Irion and Muller, 1990).

Decrease in concentration of lead experienced during pre and post monsoon seasons may be attributed to the lesser input from precipitation, comparatively sandy nature of sediment and transfer of dissolved lead to particulate phase, either by active biological uptake or scavenging / passive sorption, or by organic matter remineralization (Brugman et al., 1985; Boyle et al., 1986; Lambert et al., 1991). Organic matter remineralization was found to release metal to the water column (Regnier and Wollast, 1993). Once
released to water, dissolved lead is removed from the water column by re-adsorption onto settling inorganic particles, leading to a low dissolved metal concentration. Besides, adsorption onto particles is an irreversible process as evidenced from scavenging models of the metals (Cotte Krief et al., 2000). Several authors speculated on the adsorption of lead by sedimentary organic matter (Campbell and Evans, 1987; Seralathan, 1987; Fan et al., 2002; Nair and Ramacahndran, 2002). According to Fernex et al. (1992) a trace metal like Pb\(^{2+}\) can co-precipitate with a major dissolved metal like Mn\(^{2+}\). Adsorption of lead on surface of oxides and hydroxides of Mn and Fe is well documented (Balistrieri and Murray, 1982, 1984; Scoullos, 1986). Forstner and Wittman (1979) pointed out that under anoxic condition, lead may get co-precipitated with FeS. Besides in the present investigation lead was found to well correlate with zinc and copper as validated by regression analysis indicating their common fate in the in the mangrove sediments. 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 (Hakanson and Jansson (1983), Evans (1989). Fernex and Migon (1994) also opined that under anoxic condition, lead 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 and the very fine nature of mangrove sediments facilitates adsorption onto them and lead bound in this way would remain unaffected by physical processes such as tides and currents. Velde et al. (2003) reported the affinity of lead to clay minerals in the mangroves.

Nriagu (1978) has pointed out that environmental contamination of lead 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 industries located near the Ashtamudi Lake may contribute lead into this
system. Anthropogenic lead is mainly transported through the atmosphere (Migon, 1983; Martin et al., 1989; Guieu et al., 1998) and it is easily solubilized in water (Bethoux et al., 1990; Chester et al., 1990).

Ecotoxicological investigations revealed instances of anthropogenic inputs of lead into various riverine, estuarine and coastal environments in India and abroad (Thorne and Nickless, 1981; Bertin and Bourg, 1995; Paucot and Wollast, 1997; Guieu et al., 1998; Senthilnathan and Balasubramanian, 1999; Hatje et al., 2001). In Kerala, studies on the enrichment of lead in aquatic sedimentary environments were investigated in detail by various authors (Nair et al., 1990; Rajendran et al., 1996; Nejmi, 2000; Jayaraman, 2002). The values found herein were higher than the standard values for earth's crust (12.50 μg g⁻¹) except at Station 1 during post-monsoon. Mean lead content at all stations were lower than that of Lot river basin (France), Kaohsiung river, Taiwan and Scheldt river, France. The values observed for the rivers, Brahmaputra, Godavary, Krishna, Cauveri, Narmatha, Tapti and Subarnarekha were lower than those of the present study. Seralathen (1987) reported higher lead content in modern deltaic sediments of the Cauveri River (Table 6.1.)

Sedimentary lead exhibited significant positive correlation with sedimentary copper (Pb vs Cu- r = 0.2173, y = 114.6511 + 0.8545x, p ≤ 0.05, n = 84), Zn (Pb vs Zn- r = 0.2537, y = 100.971+0.5113x, p ≤ 0.02, n = 84), SOC (SOC vs Pb-r =0.3011 y = 7.1583+ 0.0422x, p ≤ 0.005, n = 84), and silt+ clay (Pb vs Silt+ Clay- r = 0.23 y =25.1285+0.09 x, p ≤ 0.04, n = 84), while no significant relationship was evident with sedimentary phosphorus, total nitrogen and the different organic components under investigation. It is evident from the analysis of the results that sedimentary lead in the Ashtamudi Lake might be partly mineralogical and partly anthropogenic.
in origin. Surface run off of particulate lead from automobile exhaust (Coquery and Welbourn, 1995) might be a significant input of lead into the sedimentary environment of Ashtamudi Lake.

6.3. Cadmium

Cadmium (At No. 48, At Wt.112.4) is one of the most intensively studied heavy metal with regard to its interaction with marine biological activity (Abe, 2002). Cadmium is a non-essential element of biological importance in view of its persistence in the soil environment, bioaccumulation in edible crops subsequent transfer to animals of economic importance and human beings. Cadmium is toxic and fatal to biological life even in trace quantities (Frenet and Kleeman, 1941; Schroeder, 1965). Unusual and painful disease of ‘rheumatic nature’ was recorded in the case of 44 patients from village on the bank of the Jutru River, Japan in 1947. It is estimated that approximately 100 deaths occurred due to the disease until the end of 1965. During subsequent years, it becomes known as the ‘itai-itai’ disease, meaning ‘ouch-ouch’, in accordance with the patients strikes resulting from painful skeletal deformities (Kobayashi, 1971; Hagino and Yoshioka, 1961). The first phase of poisoning is characterized by a yellow discolouration of teeth called ‘Cadmium ring’, the sense of smell is lost and the mouth becomes dry. Subsequently, the number of RBC is diminished which results in impairment of bone marrow. The most characteristics features of the disease are lumbar pains and leg myalgia, these conditions progress rapidly. Cadmium induced disturbances in cadmium metabolism accompanied by softening of bones, fractures and skeletal deformation with marked decrease in body height upto 30cm. Cadmium gets accumulated in the tissues of organisms and is supposed to damage non-regulating mechanisms. The toxicity of cadmium has created considerable interest in recent years and the metal analysis done in marine organisms firmly
established the occurrence of their metal in marine and estuarine environment. Cadmium accumulates in various parts of the body such as liver, pancreas, kidney etc.

Chemically, cadmium is an oxyphilic and Sulphophilic element. Cadmium 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. Cadmium is seldom found in a pure state in the natural environment. Geochemically, cadmium is closely related to zinc and is often found in association with zinc. All commercial cadmium is a byproduct of zinc production and there are no ores mined and processed exclusively for cadmium. It is present in various quantities in soil, water, air and food. There are many sources of cadmium in the environment viz., vegetation, air borne, soil particles, volcanogenic aerosols and forest fires contribute to natural emissions. Cadmium also enters into the air from smelters of zinc, lead, and copper, from burning of plastics, pigments, nickel-cadmium batteries, motor oil, rubber goods and tyres.

Cadmium is 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 cadmium contamination. It is therefore expected that human activities in the estuarine and coastal areas may result in relatively high concentration of cadmium (Sadiq, 1992 b). In general, cadmium enters the aquatic ecosystem via atmospheric deposition and through effluent discharges from point sources in near shore areas (Nriagu, 1980). 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 Whitefied, 1983). A high percentage of total particulate cadmium was found in the exchangeable and carbonate fractions of suspended solids in fresh waters (Moore and Ramamoorthy, 1992). Cadmium adsorbed on suspended solids in fresh water may well desorb as river water mixes with saline water. Most of the cadmium entering into the aquatic system was found to be accumulated in the sediment (Dunstan et al., 1975; Van Hook, et al., 1976). Cadmium has also been reported to be highly concentrated in and easily remobilized from sediments (Helz et al., 1975). Cadmium generally gets accumulated in the sediments reacting aquatic systems (Pedersen et al., 1989; Nair et al., 1990). This metal has an environmental behaviour similar to zinc appearing in the same fraction. Helz et al., (1975) reported that cadmium gets highly concentrated in and easily remobilized from sediment.

Sediments serve as important sink for dissolved cadmium (Lyons and Fitzgerald, 1980; Santschi et al., 1980). Sadiq (1992 b) further showed that adsorption is an important removal mechanism for cadmium from water. The most important adsorbents are organic matter, hydroxides of Fe and Mn, clays and particles of biogenic minerals. Cadmium forms moderately stable complexes with organic matter found in natural waters, including amino acids, amino sugars, polysaccharides, hydroxy and carboxylic acids of aliphatic and aromatic nature etc. which contain suitable donor atoms for complexation with cadmium (Moore and Ramamoorthy, 1992). A large variety of organic compounds is present in the sediments of mangrove. Since the mangrove sediments contain large amount of plant debris, complexation of metals with these compounds increases the metal concentration in mangroves. Affinity of cadmium for particulate matter was reported in various studies (Martin and Maybeck, 1979; Martin and Whitefied, 1983; Horowitz et al., 1996; Lead et al., 1999; Ciffroy et al., 2003). Luther et al. (1980) speculated the
formation of CdS, while, Salomons et al., 1987 concluded that trace metals like cadmium might occur as sulphides in anoxic sediments. Cadmium may precipitate as CdS in the sediments since mangrove sediments are highly anoxic. Lu and Chen (1977) further postulated that dissolved cadmium concentration was decreased under reducing conditions.

The monthly distribution of cadmium in the sediments of Ashtamudi Lake is depicted in Appendix Table 6.3. and the seasonal distribution of in Fig. 6.3. The monthly distribution of cadmium varied form 18.60 μg g⁻¹ (April) to 77.00 μg g⁻¹ (May) at Station 1; 18.40 μg g⁻¹ (April) to 69.60 μg g⁻¹ (May) at Station 2; 25.20 μg g⁻¹ (December) to 80.20 μg g⁻¹ (April) at Station 3, 11.60 μg g⁻¹ (June) to 63.80 μg g⁻¹ (September) at Station 4; 21.20 μg g⁻¹ (February) to 74.40 μg g⁻¹ (May) at Station 5; 13.20 μg g⁻¹ (May) to 73.00 μg g⁻¹ (June) at Station 6 and 19.20 μg g⁻¹ (February) to 70.80 μg g⁻¹ (January) at Station 7. Seasonal values of cadmium fluctuated between 37.35 to 53.65 μg g⁻¹; 34.28 to 51.60 μg g⁻¹ and 35.35 to 62.00 μg g⁻¹ during monsoon, postmonsoon and premonsoon respectively.

The highest concentration of 80.20 and 77.00 μg g⁻¹ was recorded at Stations 3 and 1 respectively during premonsoon may be due to increased organic matter present at these stations. Lowest value of 11.60 μg g⁻¹ found at Station 4 during monsoon followed by 13.20 μg g⁻¹ at Station 6 during premonsoon may be as a result of dilution under the influence monsoon flux. The highest annual mean concentration was registered at Station 2 among the mangrove stations.

The monsoon hike of sedimentary cadmium registered at stations 1 and 6 may be ascribed to the increase in metal rich sediments brought in by land run off at former and anthropogenic influences at the latter. Since sediments
act as a perfect sink for the metal, immediate settling of dissolved cadmium also is highly favoured. High seasonal values were recorded at mangrove stations 2, 3, and 5 during premonsoon. According to Sadiq (1992b), if physical or chemical conditions change in a system, sediment bound cadmium may be regenerated to supply the interstitial and overlying water. Temperature exerted significant influence on metal distribution at both the systems. This may be due to the increased evapo-transpiration creating more intense reducing conditions, which in turn, favours the precipitation of metal as sulphides. Lower concentration during the summer period can be due to the meager run off.

According to Elbaz Poulitchet et al. (1987), phosphate fertilizers are found to contain large amount of cadmium. Several authors confirmed the anthropogenic source of this metal (Elbaz Poulitchet et al., 1987; Valasquez et al., 2002). Piatina and Hering (2000) reported that cadmium was associated with fine particles such as clay minerals. Poultron and Simpson (1988) observed unusually high abundance of organic bound Cd in Lake Ontario sediments and Rosental et al. (1986) found a strong association between cadmium and organic matter of the sediments of the False Bay. Palanichamy and Rajendran (2000) in a study on the Gulf of Mannar sediments observed the release of cadmium from sediments to the overlying water due to the coarser nature of the sediment. Release of cadmium from suspended particles and sediments has been reported in several estuaries (Ahlf, 1983; Salomons and Forstner, 1984; Calmano et al., 1985; Mart et al., 1985). Remobilization has been explained by complexing reactions with chloride and 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 cadmium is leached from surface sediments by the process of ‘oxidative pumping’. Remobilization of cadmium during postmonsoon from surface sediments is possible as the particulate metal
Fig. 6.3 Seasonal distribution of Cadmium $\mu$g g$^{-1}$

![Graph showing seasonal distribution of Cadmium](image)

Fig. 6.4 Seasonal distribution of Zinc $\mu$g g$^{-1}$

![Graph showing seasonal distribution of Zinc](image)
concentration was high during this period. Forstner et al. (1989) shown that salinity influenced remobilization was high for cadmium. Hence, due to the increased complexation and remobilization process cadmium concentration in the estuarine sediments was low during premonsoon periods. However, the spatial and temporal variations recorded herein were not statistically significant.

Literature on cadmium content in Indian fluvial systems is scare. The values recorded herein were very high as compared to internationally accepted reference standards of average shale and earth's crust. The concentrations of sedimentary cadmium recorded in the present analysis were higher as compared to cadmium content reported in the Cochin backwaters (Nair et al., 1990), the Bharathapuzha river (Rajendran et al., 1996) and the Poovar estuary (Nejmi, 2000), other three aquatic systems in Kerala. The values were also higher than those of the Pisuerga River (Spain), the Kaohsiung River (Taiwan), the Scheldt river (France), the Vellar river and Vellar estuary and River Ganga. Cadmium content greater than that of the present study was recorded in the Lot river basin (France) by Bertin and Bourg (1995) in relation to smelting activities.

Cadmium exhibited no significant positive correlations with any of the various sedimentary factors under investigation. The study revealed that there are indications of Cadmium input onto the sedimentary environments of Ashtamudi Lake from allochthonons sources. As there are no point sources of the metal in the catchment area of the lake, urban particulates originating from the burning of plastics, pigments and paints may account for the cadmium content (Coquery and Welbourn, 1995).

6.4. Zinc

Zinc (At. No. 30, At. Wt. 65.39) is one of the most abundant biologically essential trace element in the human body and approximately hundred times
as abundant as copper and it is a metal moiety of about 70 metalloenzymes (Vehrenkump, 1973; Vallee, 1978). It plays a vital role in the biosynthesis of nucleic acids, RNA and DNA polymerases. Zinc plays a dual role as a micronutrient and as a toxicant depending on its bioavailable concentration in any biological system. This element is an activator for certain enzymatic reactions and also functioning as a co-factor for the enzyme carbonic anhydrase. The growth of certain phytoplankton is affected as zinc is insufficient in the aquatic medium. Zinc is being applied to agricultural soils as Zinc sulphate, Zinc chloride and Zinc oxide, in view of its importance in plant nutrition. Zinc sulphate (ZnSO$_4$.7H$_2$O) is the only zinc source being manufactured commercially for agricultural use in India. The main source of zinc in aquatic system is runoff from agricultural soils and through industrial effluents, urban wastes and sewage (Dean et al., 1972). The main pollutant sources of zinc are metalliferous mining activities, ore-dressing and processing, agricultural use of sewage sledge and the application of agro-chemicals such as fertilizers and pesticides.

The environmental chemistry of this element was reviewed in detail by Kiekens (1990). Zinc occurs in nature as Zinc blende, Zinc sulphide, Zinc silicate, Zinc spar, Zincite (ZnO) etc. Zinc salts are relatively nontoxic but heavy doses (165mg) for a period of 26 days cause vomiting, renal damage and cramps (Kudesia, 1990). It is also able to bioaccumulate and hereby poses a potential threat to the food chain.

A number of works have been reported on the behaviour of zinc in aquatic systems. Zinc is considered to act in conservative manner in large unpolluted estuarine (Holliday and Liss 1976; Elderfield et al., 1979; Danielson et al., 1983), whereas it may behave in a nonconservative manner in polluted estuaries (Duinker and Nolting, 1982; Paul and Pillai, 1983; Duinker
et al., 1985; Ouseph, 1987; Campbell et al., 1988; Nair et al., 1990). Sankaranarayanan et al., 1978; Paul and Pillai, 1983; Brook and Moore, 1988 Shibu et al., 1990; Perin et al., 1997; and Wihams et al., 2000 reported considerable anthropogenic input of zinc into the Cochin estuary. Most of the zinc was found in the dissolved phase in fresh water while the amount of zinc was found reduced in estuarine waters (Shibu et al., 1990). Nair et al. (1990) observed significant seasonal and spatial variation in the distribution of zinc in the surficial sediments of Cochin backwaters. Senapati and Sahu (1996) recorded strong enrichment of zinc in the sediments of the Subarnarekha river. Thus, incorporation into the sediments as metal sulphides may be another pathway for zinc in the anoxic environments. Moreover, several authors reported that elevated metal concentration related to long-term pollution caused by human activities in mangrove sediments (Mackay et al., 1992; Lacerda et al., 1993; Tam and Yao, 1998). Similarly, different studies showed that mangrove sediments have a high capacity to retain trace metals from tidal water and therefore they act as sink for trace metals (Harbison, 1986; Lacerda et al., 1993; Tam and Wong, 1993, 1995).

Earlier studies showed wide variations in zinc concentration. Zinc content varying from 43.56 to 940.46 μg g⁻¹ was registered by Rini (2002) in the Vypeen mangroves, while Badarudeen (1997) recorded lower values ranging from 15.00 to 91.00 μg g⁻¹ in the same area. Seralathan (1987) observed zinc concentration varying between 76.00 -107.00 μg g⁻¹ in the Cauvery mangrove sediments. However, much higher zinc concentrations were reported in the sediments elsewhere. Zinc content ranged between 46.40 to 347.80 μg g⁻¹ in the mangrove sediments of south east Gulf of California (Soto-Jimenez and Paez-Qzuna, 2001) whereas, Ong Che (1999) observed much higher zinc concentration in the Mai Po mangroves, Hong Kong, where it varied from 148.00 to 513.00 μg g⁻¹.
Metal enrichment in the sediments can be related to its removal from solution by terrestrial organic matter, which eventually becomes incorporated in the sediment. Maximum concentration of the metal during monsoon period may be the result of heavy influx of metal rich particulates associated with the run off waters. According to Hong et al. (1994), zinc has moderate binding capacity with humic acid and fulvic acids and they observed that 93 - 98 % of Zn was complexed by organic matter in the interstitial water as a result of high ligand concentration.

The seasonal distribution of zinc in the sediments of Ashtamudi Lake is depicted in Fig. 6.4. and the monthly distribution in the Appendix Table 6.4. The monthly distribution of zinc varied from 11.00 µg g⁻¹ (November) to 76.60 µg g⁻¹ (February) at Station 1; 25.20 µg g⁻¹ (August) to 85.40 µg g⁻¹ (November) at Station 2; 76.00 µg g⁻¹ (March) to 124.40 µg g⁻¹ (May) at Station 3; 22.20 µg g⁻¹(July) to 94.20 µg g⁻¹(May) at Station 4; 21.80 µg g⁻¹(March) to 65.80 µg g⁻¹(May) at Station 5; 41.40 µg g⁻¹(May) to 113.40 µg g⁻¹ (November) at Station 6 and 24.00 µg g⁻¹(November) to 66.40 µg g⁻¹(May) at Station 7.

The seasonal concentration of zinc fluctuated between 33.25 µg g⁻¹ (Station 4) and 99.90 µg g⁻¹ (Station 3); 31.55 µg g⁻¹ (Station 1) and 96.45 µg g⁻¹ (Station 3) and 40.30 (Station 1) and 89.60 µg g⁻¹ (Station 3) during monsoon, postmonsoon and premonsoon periods respectively. The highest values of 124.40 µg g⁻¹ was recorded at Station 3 during premonsoon and 113.40 µg g⁻¹ at Station 6 during postmonsoon may be due to the enhanced organic matter present at these stations. The higher seasonal values were recorded at Stations 3 and 6 during monsoon and postmonsoon period and the lowest at Station 1 during postmonsoon. The lowest amount may be due to the sandy nature of the sediment coupled with desorption of the metal under marine influence. Distribution of sedimentary zinc content in the Ashtamudi Lake showed significant stationwise variations (ANOVA: \( F = 20.7273; \)

\( d.f. = 6; \ p \leq 1.7256E-13 \) however, temporal variations were not statistically significant. The annual mean value of zinc in non-mangrove area is comparatively lower than that of mangrove site. The textural characteristic as well as the organic matter content of the sediment influenced the concentration of zinc in the mangroves.

Microbial degradation of the huge amount of organic matter in mangroves mud generally utilizes all oxygen from sediments below the surface layer, creating an 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 on metal humate complexes are then deposited as sulphides (Pauli, 1975). The values of sedimentary zinc in the present study remained lower than that of average shale and earth crust, while the values were higher than that of Indian average (Table 6.1.). The concentration of zinc was also lower than that of value recorded in the sediments of the Cochin backwaters (Nair et al., 1990), and higher than rivers Bharathapuzha (Rajendran et al., 1996) and Pumba (Mathew Koshy, 2001). Subramanian et al. (1985) suggested higher amounts of zinc content in the sediments of different rivers such as Ganga, Brahmaputhra, Godavari, Krishna, Narmatha, Tapti and Cauvery and Vellar estuary (Mohan, 1997) as compared to the present investigation. Sedimentary zinc content in aquatic systems abroad viz., the Yarra river estuary, Australia (Smith and Milne, 1979), the Scheldt River, France (Paucot and Wollast, 1997) and the Pisuerga River, Spain (Pardo et al., 1990) were also higher, as compared to present study. The sedimentary zinc content observed in the Poovar aquatic system (Nejmi, 2000) remained within the range of the present investigation.
On an annual basis, maximum enrichment was observed at Station 3 and 6. Stations 4 and 7 are located at the estuarine zone affected by tidal fluxes where the sediment was of sandy texture. Station 6 is influenced by sewage inputs brought in by anthropogenic activities. The sedimentary environment of Ashtamudi Lake may possibly be free from pollution by zinc reflecting only the background levels.

In the present investigation zinc showed significant positive correlation with lead (Zn vs Pb - $r = 0.2537$, $y = 100.971 + 0.5113x$, $p \leq 0.02$, $n = 84$), sediment organic carbon (Zn vs SOC - $r = 0.6858$, $y = 1.8794 + 0.1934x$, $p \leq 6.09E-13$, $n = 84$), silt + clay (Zn vs Silt + Clay - $r = 0.7546$, $y = 2.4533 + 0.6300x$, $p \leq 1.14E-16$, $n=84$), sedimentary carbohydrates (Zn vs CHO - $r = 0.5816$, $y = 0.8653 + 0.0468x$, $p \leq 6.59E-09$, $n = 84$), sedimentary protein (Zn vs Protein - $r = 0.5228$, $y = 0.3830 + 0.0209x$, $p \leq 3.35E-07$, $n = 84$) and sedimentary lipids (Zn vs Lipid - $r = 0.2719$, $y = 0.1522 + 0.0047x$, $p \leq 0.01$, $n = 84$), while no significant relationship was evident with cadmium, sedimentary phosphorus, total nitrogen and hydroxylated aromatic compounds. The results of correlation studies suggested mineralogical as well as organic associations of zinc.

In general, the study on trace metal distribution in the sediments of Ashtamudi Lake revealed that maximum enrichment of metals occurred in sediment at Station 3 where the precipitation of metal may be due to mixing of river water with saline water. The study suggested that the influx of water, transport metals as well as nutrients in the Ashtamudi Lake to a large extent.

Knowledge of the sources of toxic elements and their relative abundance is necessary for effective control measures to prevent pollution.
The metal concentration in sediment is depended on the nature, adsorption and retention capacity of the substratum, apart from the effect of flocculation and coagulation causing the particulate matter to settle down to the bottom. The metal enrichment in the sediments is related to the removal of metal from the solution by terrestrial organic matter which eventually becomes incorporated into sediment (Lorne, 1978).

The present study showed high amounts of lead in the sediments collected from all the stations. Considerable quantity of zinc and cadmium were also present. However, the copper content was found much less. The high concentration of metals observed may be due to the discharge of metals from agriculture, containing fertilizers, pesticides and rodenticide residues, weathering of rocks etc. The concentration of lead was low as the sources for these metals were found lacking on the vicinity of the study area. The metal levels observed in the present study is within threshold limits (Senthilnathan and Balasubramanian, 1999). However, as these metals are capable of posing threat over a period of time, present levels of contamination has to be dealt with great concern.

Information on the levels of trace metal pollution in the environment is important as they cause serious environmental health hazards. These elements are magnified in the food chain and reach human beings causing deleterious effects. The present study further implies the need for continuous regular monitoring of coastal waters, which are vulnerable to metal pollution. The study revealed that the lake is relatively free from contamination by metals such as Cu, Pb, Cd and Zn may be due to the absence of any point sources such as major and minor industries. However, there are indications of contamination by lead and cadmium, the metals of considerable ecotoxicological significance.
The maximum trace metal flux was experienced during monsoon in the case of copper and zinc while the others, lead and cadmium during premonsoon. Significant monthwise, season wise and stationwise variations were evident in all cases. Spatial as well as temporal environmental variables have significant influence in regulating metal content in the sediment of the lake. Spatial variability may be attributed to the change in relative contribution of sediments draining from different geological formations and sorting of size fractions during transport process and human influence (Ramesh et al., 1990). In the present study the only possible non-point sources of metals were agricultural inputs, domestic effluents and air borne particulates of urban origin settling in the catchment area.

6.5. Contamination factor for trace metals

Contamination factor has been calculated using trace metal concentration data. It is expressed as metal concentration in the sediment divided by the back ground value of that metal (Turkian and Wadephol, 1961). The world average value for shale is taken as the back ground value. In the present investigation contamination factor values for copper, lead, cadmium and zinc are 0.38, 6.46, 154.90 and 0.58 respectively. Since the values remained<1.00 for copper and zinc, no point source need be mentioned for these metals. High value observed for lead indicated incidence of anthropogenic inputs. Burning of plastics and fossil fuels is the common phenomenon in the urbanized life style may be the reason for high cadmium concentration in the sediments of Ashtamudi Lake.

Geochemistry of Sediment in the Ashtamudi Lake compared with other Indian and foreign water bodies and sediments (Table 6.1).
### Table 6.1

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