Impact of Tsunami on the Biogeochemical Changes in the Sediments of Pichavaram Mangroves, SE Coast of India - Post Tsunami Scenario

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CERTIFICATE

This is to certify that the research work embodied in this dissertation entitled "Impact of Tsunami on the Biogeochemical Changes in the Sediments of Pichavaram Mangroves, SE Coast of India-Post Tsunami Scenario" has been carried out by Mr. Rajesh Kumar Ranjan in the School of Environmental Sciences, Jawaharlal Nehru University, New Delhi under supervision of Dr. AL. Ramanathan, for the partial fulfillment of the award of degree of Master of Philosophy.

This work is original and has not been submitted in part or full for any other degree or diploma in any other university and institution.

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Dedicated to the poor souls who lost their lives
and
to those who lost their livelihood

CONTENTS

Pages

Appendices

LIST OF TABLES

LIST OF FIGURES

Chapter 1

Introduction

Mangrove are the woody community that can be periodically submerged in seawater of the inter-tidal zone of tropical and subtropical regions (Lu and Lin, 1990). They are the second highest source of primary production next to rainforests (Singh et al., 2005). They produce high detritus and release nutrients, which are food source for various organisms. They provide homes to variety of marine and terrestrial organisms. They act as nurseries and feeding grounds for many fish, shrimp and crustaceans and non-resident fish enter the mangroves to feed at high tide. Mangroves are also prime nesting and migratory sites for hundreds of bird species. They not only provide a wealth of biodiversity, but also are an essential part of the world's food web.

These important inter-tidal estuarine wetlands are exposed to anthropogenic contamination from tidal water, river water and land-based sources (Klekoski et al., 1994) as well to the natural calamities. As with most ecosystems, an intricate relationship exists between mankind and mangrove. They have several ecological, socio-economical, and physical functions that are essential in maintaining biodiversity and protecting human populations. Many indigenous coastal residents rely on mangroves to sustain their livelihood and traditional cultures. Mangroves are sustainably used for food production, medicines, fuel wood, fishery, honey and construction materials (Singh et al., 2005). Their complex architecture, combined with their location on the edge of land and sea, makes mangrove forests strategic greenbelts that have a doubly protective function. They protect seaward habitats against influences from land, and they protect the landward coastal one against influences from the ocean.

Mangroves are adapted to intertidal environmental conditions such as high-energy tidal action, high salt concentrations, and low levels of oxygen (hypoxia). The large aboveground aerial root systems not only offer improved breathing for the plant but also protect more seaward and more landward areas. The important biogeochemical services of mangroves include the entrapment of sediments and pollutants, filtering of nutrients, remineralization of organic and inorganic matter, and export of organic matter. Mangroves also function as carbon dioxide sinks by removing and storing carbon dioxide from the atmosphere, which is a major contributor to global warming. Mangrove degradation has been associated with a decline in the function of lagoon and offshore fisheries, which most fishing communities rely on to provide their main supply of dietary protein.

1.1 Global Distribution of Mangroves

Mangroves are distributed globally occurring in 112 countries and territories. Total global mangrove coverage is 18 million hectares and it is just about 0.45% of world forests & woodland (Spalding, 1997). Of the total mangrove coverage, 41.4%' exist in South and Southeast Asia. Mangroves are largely restricted to latitudes between 30° N and 30° S. Northern extensions of this limit occur in Japan (31°22' N) and Bermuda (32°20' N); southern extensions are in New Zealand (38°03' S), Australia (38° 45' S) and on the east coast of South Africa (32°59' S) (Spalding, 1997).

1.2 Status of Mangroves in India

Indian mangroves are distributed in about 6,740 sq.Km (Fig. 1.1) which constituted 7% of the total Indian coastline (Krishnamurthy et al., 1987). The area-wise distribution of mangrove forests in India has been reviewed (Deshmukh, 1991a). Status of mangroves along the Arabian sea has been reviewed (Untawale, et al., 1992). There are three different types of mangroves in India viz., deltaic, backwater-estuarine type of mangroves existing in the west coast **(Table 1)**, characterized by typical funnel-shaped estuaries of major rivers (Indus, Narmada and Tapti) or backwaters, creeks, and inlets. The insular mangroves are present in Andaman and Nicobar islands where many tidal estuaries, small rivers, neritic islets, and lagoons which support a rich mangrove flora (Gopal and Krishnamurthy, 1993). Of the Country's total area under the mangrove vegetation, 70% is recorded on the east coast, and 12% on the west coast. The bay islands (Andaman and Nicobar) account for 18% of the Country's total mangrove area (Krishnamurthy et al., 1987; Kathiresan, 1995a). The mangroves have a vast existence on the east coast of India due to the nutrient-rich alluvial soil formed by the rivers – Ganga, Brahmaputra, Mahanadhi, Godavari, Krishna and Cauvery and a perennial supply of freshwater along the deltaic coast. But, the deltas with alluvial deposits are almost absent on the west coast of India, only funnel – shaped estuaries or backwaters are present (Gopal and Krishnamurthy, 1993). The deltaic mangroves on the east coast are about 57% (2,738 km^2) of the country's total area of mangroves. The insular mangroves exist in the Bay islands (Andaman and Nicobar) on many tidal estuaries, small rivers, neritic islets and lagoons, accounting for 20% (383 km^2) of total Indian mangroves.

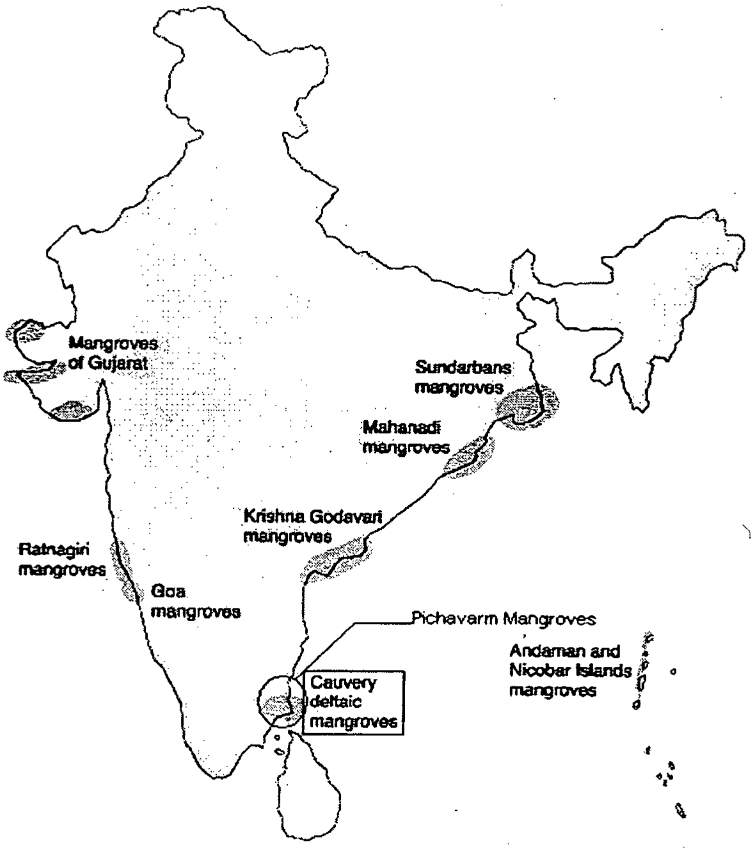

Fig. 1.1: Map of Mangrove ecosystems of India

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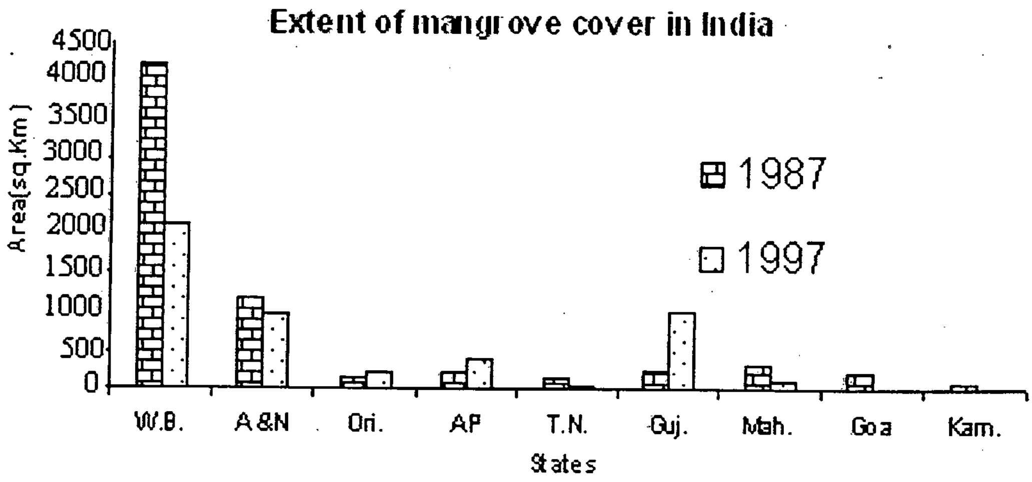

Fig. 1.2: Extent of Mangrove ecosystems of India

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Table 1.1 Environmental setting of mangroves of India (Thom, 1984)

Mangrove	Setting	Dominant features
Sundarban and Bhitarkanika mangroves	Tide dominated allochthonous type of mangroves	High tidal range with strong bi directional current; main river channels funnel shaped with extensive tidal flat, colonized by mangroves.
Krishna and Coringa mangroves of Andhra Pradesh and Pichavaram and Muthupet of Tamilnadu	River dominated allochthonous type of mangroves	Rapid deposition of terrigenous material; delta expand sea wards, mangroves dominate in the region of abundant delta found near by without mangrove vegetation.
Gulf of Kutch and Gulf of Khambat mangroves of Gujarat	Drowned bedrock velley type of mangroves	Bedrock valley drowned by rising sea level, relatively small delta area could be seen at the head of the valley, tidal delta may occur in the mouth of estuary.
Andaman and Nicobar Island mangroves	Carbonate platform on low energy coasts type of mangroves	Platform slowly accreting due to the accumulation of marl (calcareous) and peat, coral reef or sand barrier mitigate wave energy and allow fringe mangrove to grow extensively in shallow water area

However, the extent of mangroves keeps on changing over a period in different states of the east coast and the Bay Islands. The satellite data between 1993 and 1997 revealed a considerable increase in mangrove cover: 31.13% in West Bengal; 25.4% in Bay Islands; and, 12.83% in Orissa and a reduction in mangrove cover in other states: 76.7% in Tamil Nadu; and 20.21% in Andhra Pradesh (Kathiresan, 2000). Of 35 mangroves plant species, 9 are critically endangered, 23 endangered and 3 vulnerable (Rao et al., 1998).

Mangroves in Tamil Nadu exist on the Cauvery deltaic areas. The total mangrove area available in this state is around 383 sq.km (Kathiresan, 1998). Pichavaram mangroves that extend between the Vellar and Coleroon estuarine areas, spread to an area of 21 sq.km (Kannan, 1990). Pichavaram has a well developed mangrove forest dominant with *Rhizophora* spp., *Avicennia marina,Excoecaria agallocha*, *Bruguiera cylindrica*, *Lumnitzera racemosa*, *Ceriops decandra* and *Aegiceras corniculatum* (Kathiresan, 1998). It is a highly populated region, but the mangrove is relatively well preserved because it enjoys the status of a Reserve Forest since 1880. These mangroves are noteworthy for their beauty, luxuriance and diversity of species (Meher Homji, 1991).

1.3 Significance of Mangroves

1.3.1 Ecological Significance of Mangroves

Ecological importance of the mangrove areas as breeding, nursery and feeding for crustaceans, fishes and birds is well documented. Recent observations have revealed the environmental importance of mangrove areas in beach protection against erosion and as buffer zones for protecting adjacent marine ecosystems from excessive terrigenous particle and chemical loading. Studies generally show that mangrove forests are outwelling systems in terms of dissolved, particulate and macro detritus. Hydrodynamics and geomorphology of the shore to a great extent influence the exchange of material between the forest and the adjacent inshore water. Considering the high productivity of mangrove areas and their ecological role as efficient natural filters for terrestrial run off.

1.3.2 Social-economic Significance of Mangroves

Direct and indirect uses of mangrove species may include; source of medicines, honey, sugar, vinegar, alcohol, fuel and intoxicating local beverage. Commercial products include timber for construction, poles for fish traps, wood pulp for paper manufacture and wood chip production (Chapman, 1976). Intangible benefits from mangroves are many, including growing grounds for juvenile fish and crustaceans. Mangrove forests offer home for variety of wildlife, which is one of main tourism, ecotourism. Apart from these, mangrove sediments act as sinks for nutrients and heavy metals (Alongi, 1996). Mangrove sediments, therefore, prevent eutrophication and development of toxic concentrations of pollutants in inshore waters. Because of this, mangrove forests have previously been used as efficient, coast effective sewage treatment facilities.

1.3.3 Role of Mangroves against natural calamities.

Mangroves protect sea grasses and coral reefs by trapping sediments and nutrients from overland fresh-water sources that would otherwise be deposited more seaward and cause turbidity and/or eutrophication (excessive nutrient concentration with periods of oxygen deficiency). On the other hand, mangrove trees can protect the landward area against the fury with which meteorologic or oceanologic processes, such as cyclones or tsunamis, may strike. Mangrove tree species that inhabit lower tidal zones, such as *Avicennia* spp. (Grey or Black mangrove) or *Sonneratia* spp. can block or buffer wave action with their stems which can measure 30 m (100 ft) high and are several meters in circumference. Mangroves maintain a climate and pollution record, and they provide educational and scientific information from which we can learn. It has been estimated that the total mangrove surface area has decreased from 1,98,090 km^2 in 1980 to 1,48,530 km^2 in 2000, a 25% loss. This impact has been documented through retrospective sequential remote sensing, interviews with local people, and archive research—which all indicate that major mangrove functions have been lost. In turn, this loss of natural functions has considerably exposed the natural environment to stochastic oceanic or climatic events such as cyclones and tsunamis.

1.4 Causes of Mangrove Degradation

There are various factors contributing towards the degradation nature-induced changes as well as anthropogenic contribution (Fig. 1.3). These devastation has caused a significant decrease in the mangrove are cover in past few decades

1.4.1 Anthropogenic inputs

Urbanization

Urbanization is one of the most important reasons for the degradation of mangrove. These coastal wetlands have been cleared for human inhabitation in many areas like Singapore, Jakarta, Bangkok, Rangoon, Kolkata (Calcutta), Mumbai (Bombay), Lagos, Maracaibo, Recife, Free town, Douala *etc.* .In India, Mumbai is one of the best examples for the mangrove destruction due to urbanization. (Kathiresan, 2005). All the seven islands of Mumbai were reclaimed are now linked to a continuous landmass after destroying mangroves in the process. In Pichavarm over the last decade the mangrove forest cover has ben decreaseing on the cost of human development. The forest cover (Fig. 1.4 and 1.6) has decreased from 4.9 sq Km (1970) to 3.7 sq Km in 1996 (Yeon CHO et al., 2004).

Agriculture

The history of restriction of Sundarbans is nothing but the history of conversion of mangrove forests for agricultural purposes. This reclamation process was initiated in 1770 and it continued till recent past. In the largest delta region of the world, existing between India and Bangladesh, 1,500 sq.km of mangroves were destroyed during the past 100 years, and these were mainly reclaimed for agriculture. The mangrove areas are deforested and reclaimed with rainwater to intrusion by constructing embankments. Once the salt is leached to a sufficient level, the land is cultivated either with paddy or coconut. In the past decades (1970-1996), no significant variation in the agriculture land cover has been observed around Pichavaram mangrove(Fig. 1.4 and 1.6). However, the crop cultivation pattern has changed thus causing stress to already fragile ecosystem (Yeon CHO et al., 2004; Kathiresan, 2005)

Aquaculture practices

A large-scale destruction of mangroves was made for aquaculture in several countries. To cite an example, in the Philippines, between 1968 and 1983, 2,370 sq. km of mangroves were lost for pond construction. This is almost half of the total national mangrove area (Fernandez, 1978). One major issue associated with the farms located in mangrove habitats is acidification of pond waters that kills aquatic organisms. In Ecuador, the decline in mangrove areas was largely due to the construction of 215.87 sq.km of shrimp ponds, compared to only 11.57 sq.km for urban expansion in 1969-84. In Thailand, around 50% of the total denuded mangrove

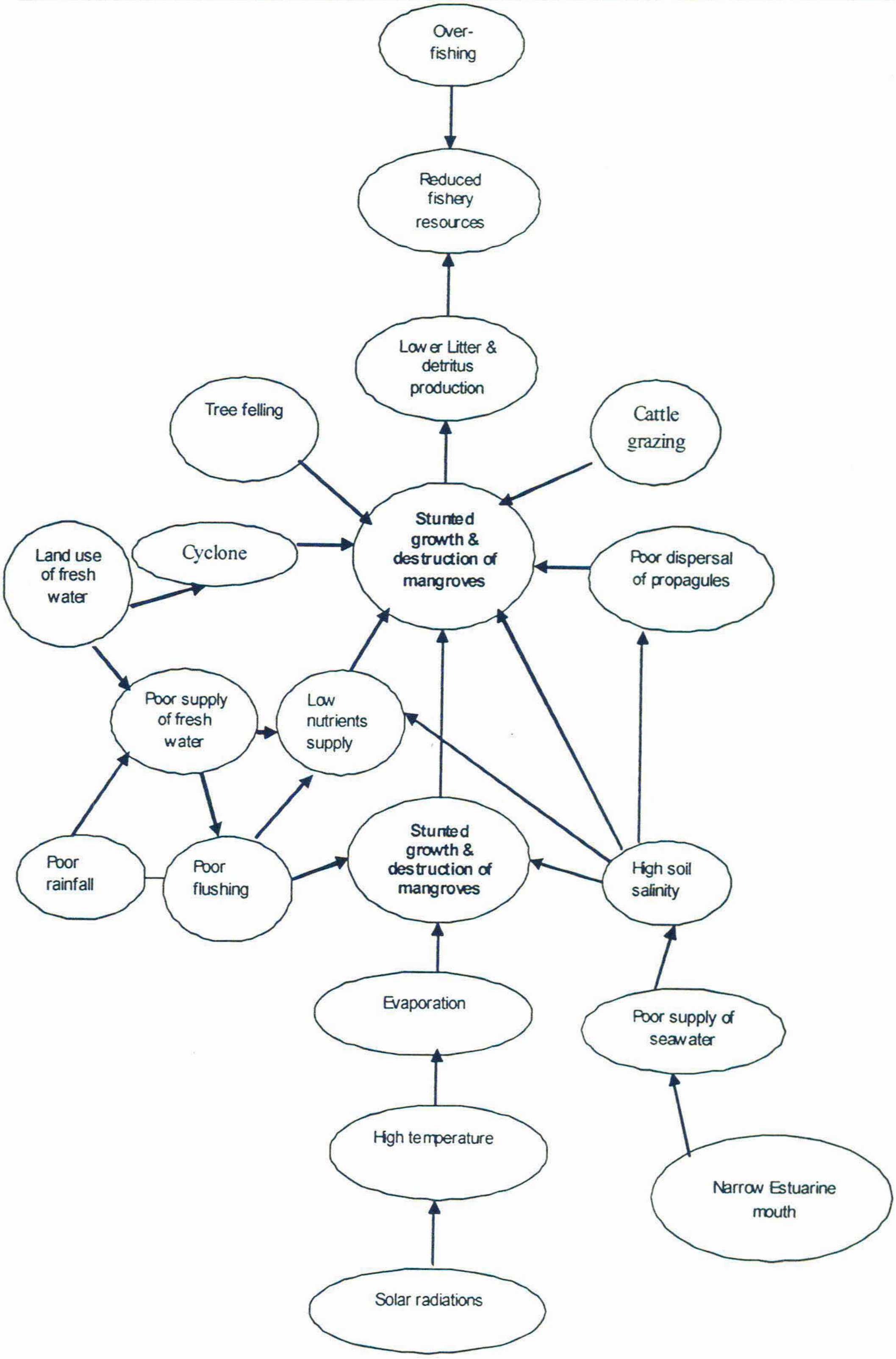
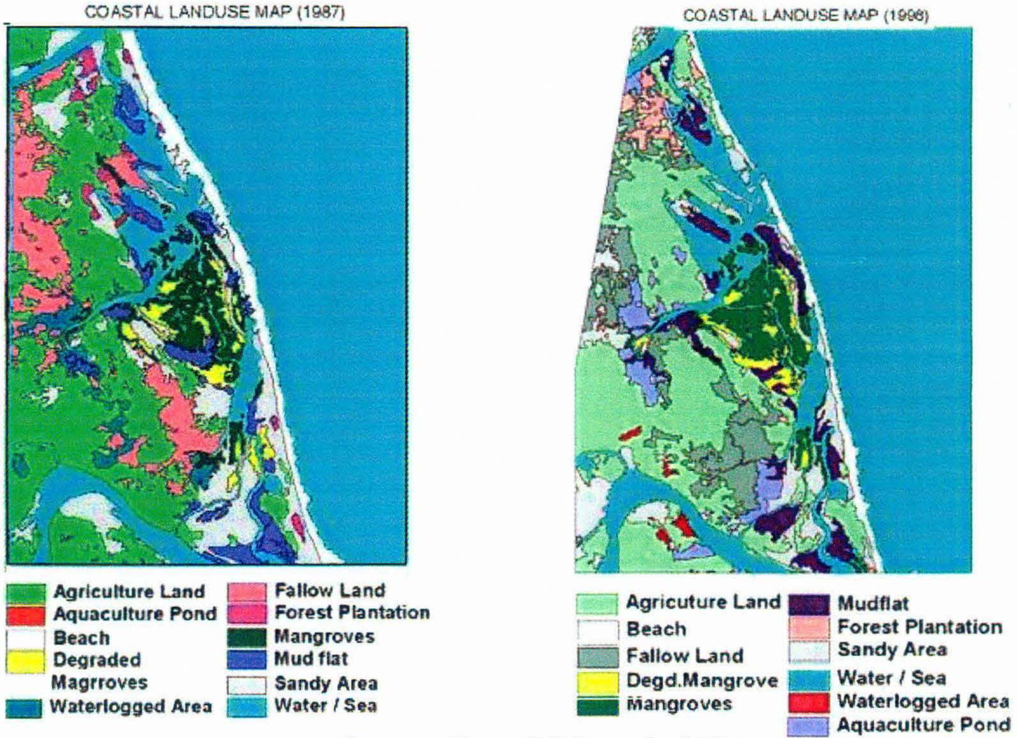


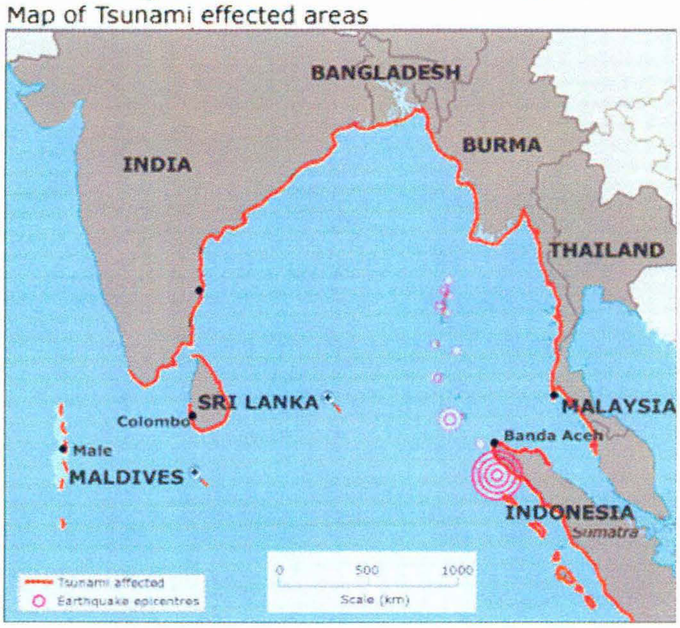
Figure 1.3 Causes of Mangrove degradation (Kathiresan, 2005)

Fig 1.4 Map of Land use pattern around Pichavaram Mangrove ecosystem(1987, 1996)



Source: Yeon CHO et al., 2004

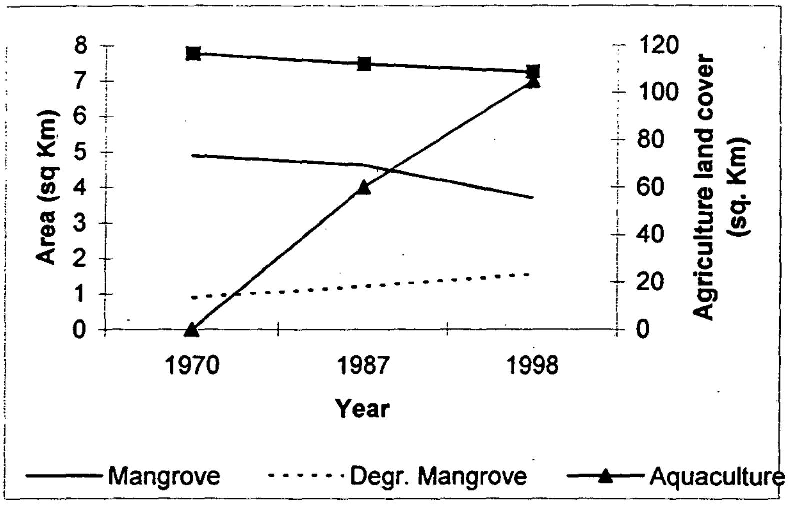
Fig. 1.5 Tsunami inundated areas



Source: Map Asia Conference 2004

area of 1714.72 sq.km was converted into aquaculture ponds during the period 1961-87. Pichavaram stands a good example for the degradation of mangrove due to aquaculture practices. During 1970s, there were no aquaculture ponds in the area, whereas in 1984 it increased to 3.99 sq Km and in 1996 to 6.99 sq km (Yeon CHO et al., 2004; Kathiresan, 2005)

Fig. 1.6 Changes in land use pattern in Pichavaram mangroves over past decades (1970-1996)



Source: Yeon CHO et al., 2004

1.4.2 Natural facture responsible for the degradation of mangrove

Tropical storms and cyclones are common in the Bay of Bengal and the Caribbean Sea and destruction of Bhitarkanika mangrove forest due to the cyclone is well documented (Kathiresan, 2005).

Diseases also cause devastating damages to mangroves. For example, top dying disease has damaged about 45 million *Heritiera fomes* (Sundari) trees. This is about 20% of the entire forests in Bangladesh (Hussain & Acharya, 1994). The top dying disease is believed to be caused by an array of factors -- increased soil salinity due to reduced water flow, reduction in periodic inundation, excessive flooding, sedimentation, nutrient imbalances, pathogenic gall cankers, and cyclone - induced stress.

Biological pests and parasites also have serious impacts on mangroves. Significant damage is caused by grazing of buffaloes, sheep, goats and camels in dry coastal areas of Asia and the Middle East. Young plants are damaged by barnacles and leaf eating crabs of the sesarmid family. Some caterpillars are parasites of the fruits of Rhizophora, and these inhibit seed germination.

1.5 Tsunami 2004 and the role of mangroves

The tsunami of December 26, 2004 has caused economic and ecological disaster in 13 Asian and African Countries (Fig.1.5). The sea waves were generated due to massive undersea earthquake, measured at 9 in the Richter scale, off Sumatra in Indonesia. It is estimated that about 1,200 km of the Burma plate forced a massive displacement of water in the Indian Ocean. This motion generated waves that spread in all directions, moving as fast as 800 km hr^{-1}. Waves up to 30 m (100 ft) high were reported to have stripped beaches with tourist resorts, local houses, roads, railways, and other human infrastructures and settlements up to several hundred meters or even several kilometers inland. Recurrent high waves and the receding waves caused a massive flow of water and debris that ravaged the coastal zone. In total about 2,95,000 deaths and 130,000 injuries were recorded thus affecting 53 countries directly or indirectly. Until December 25, 2004, the most destructive tsunami that ever occurred in the Indian Ocean resulted from the eruption of the Krakatau (Krakatoa) volcano in 1883. The Krakatau explosion and resulting tsunami claimed around 36,000 human lives on Java, Sumatra, and smaller islands scattered on the Sunda Strait (Indonesia). But on December 26, the South-East Asia tsunami struck, resulting in tenfold more deaths, than the Krakatau volcanic eruption and leaving millions homeless. The monstrous waves have killed more than 0.2 million people, made about 2 millions home-less. In India, Coastal forests and agriculture lands were destroyed in several tsunami-hit areas. The affected parts of the forests were mostly seedlings, less dense forests, narrow strips of forests and the aerial roots that are clogged with silt deposits. In India, tsunami-hit Nagapattinam suffers the damage of 15,000 acres of agricultural land along with paddy and' groundnut crops, due to intrusion of seawater inland.

However, it seems that the coastal communities inhabiting behind the mangrove forests largely escaped from the fury of the tsunami. In Indonesia, the epicenter of the Dee. 26 tsunami was closer to Simeuleu Island, however, the death toll on this island was significantly low because of presence of very good mangroves there and this country has planned to revive its coastal defenses, ear-marking some 600,000 hectares of mangroves across the country, which has lost 30% of its mangrove forest, cover

over the past several decades. The dense growth of mangroves saved thousands of kilometers of Sundarbans in India and Bangladesh from the killer impact of tsunami.

In Thailand, the Island chain of Surin off the west coast escaped heavy destruction because the ring of coral reefs and mangroves that surround the Island helped break the lethal power of the tsunami. In and around the Yale national Park, Sri Lanka, where the tsunami waves were very strong and there were no physical barriers present such as sand dunes, the mangroves and scrub jungle bored the full fury of the Tsunami .In southern part of India, there were only low human causalities and less economic damage at Pichavaram and Muthupet with dense mangrove forests.

A study was conducted by Kathiresan et al., (2005) after the recent tsunami in 18 coastal forests (Fig. 1.7), located at a distance ranging from 1 to 2.5 km away from the shoreline and that are in elevated places with steep topography due to the presence of sand dune communities in between the hamlets and shoreline. However, heavy loss of human lives was recorded in mangrove-less hamlets that are in close proximity to the shoreline (between 0.1 and 0.4 km) and that occur in low-lying areas of smooth topography. The tsunami caused human-kill increased with wealth loss and decreased Unfortunately the role of mangroves as living barriers was under appreciated prior to the tsunami event of December 2004, and many mangrove forests had already been destroyed or damaged. This was the case for many mangrove sites in East Africa, Thailand, Indonesia (for example, Banda Aceh), India, and Sri Lanka (for example, the southwest coast)—areas badly affected by the tsunami tragedy. Mangrove forests play important in reducing the fury caused by the tsunami. The measurement of wave forces and modelling of fluid dynamics suggest that tree vegetation may shield coastlines from tsunami damage by reducing wave amplitude and energy (Massela et al.1999). Analytical models show that 30 trees per 100 m2 in a 100-m wide belt may reduce the maximum tsunami flow pressure by more than 90% (Hiraishi et al.,2003). An assessment of coastlines after the tsunami indicates that coastal vegetation such as mangroves and beach forests helped to provide protection and reduce effects on adjacent communities. Danielsen et al., (2005) had highlighted that mangroves and *Casuarina* plantations attenuated tsunami-induced waves and protected shorelines against damage. He suggested that conserving or replanting coastal mangroves and greenbelts should buffer communities from future tsunami events.

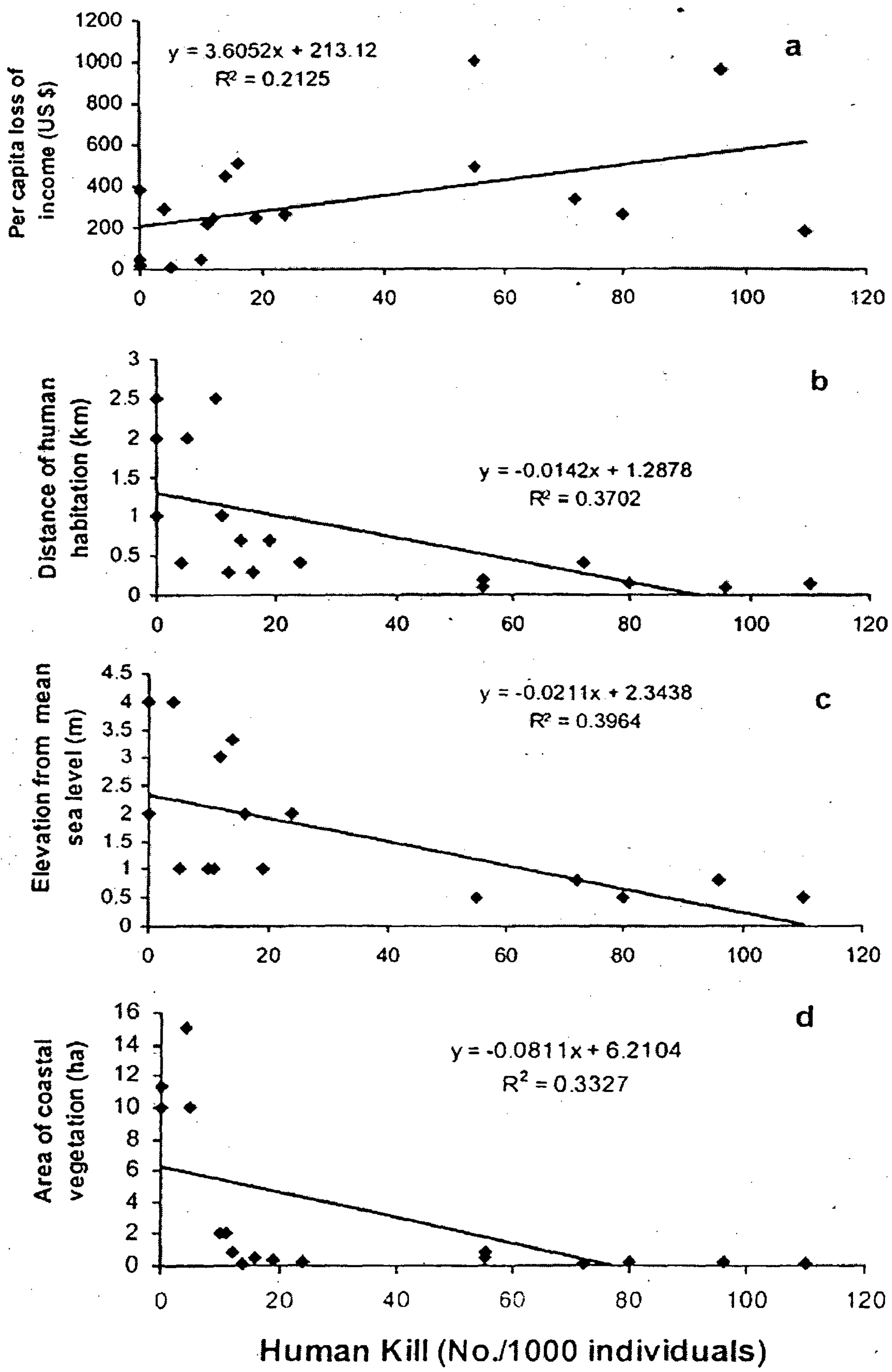


Figure 1.7 . Impact of Tsunami showing the influence of Caostal vegataion on human kill (Kathiresan, 2005)

Further, Tsunami waves are known to be able to cause significant alterations in coastal systems (e.g. Dawson, 1994; Bryant et al., 1996; Bryant, 2001; Scheffers and Kelletat, 2003). They may produce extensive changes in coastline topography: considerable erosion and subsequent deposition of substantial quantity of sediments in short time span. Tsunami also through translation of large amount of seawater on land—introduces salt into surface and ground waters and, in consequence, does have substantial impact on coastal ecosystems Its effects, however, are not restricted to the damages due to direct impact of the wave but they also include some long-term consequences. The latter comprise problems associated with soil contamination by seawater and tsunami sediments, which may contain some pollutants released due to damages of waste disposal storages, factories, fuel stations, etc. Only in Thailand, about 20,300 ha of land were covered by seawater during that event. Most of that area was also covered with a blanket layer of tsunami sediments (Szczucin'ski et al., unpublished data). In spite of a number of studies focused on contemporary tsunami sediments (e.g. Nishimura and Miyaji, 1995; Shi et al., 1995; Dawson et al., 1996; Dawson and Shi, 2000; Nanayama et al., 2000; Gelfenbaum and Jaffe, 2003), the aspects of their contamination and possible source have been worked out rarely.

Therefore the present work was under taken with following objectives to assess the impact of tsunami on the Pichavaram mangrove ecosystem.

- To assess the nutrient dynamics in water of the Pichavaram ecosystem.
- To study the biogeochemical variability of the macronutrients (C, N, P and S), micronutrients (Fe, Si, Zn, etc.) and heavy metals.
- To understand the distribution, fractionation and their trophic states of Phosphorus (P) in the mangrove sediments
- To lay bare the grain size variation of the mangrove sediments and its control on the nutrient distribution.
- To assess the pollution status using metal fractionation studies.

Chapter 2

Review of Literature

Processes that generate sedimentary features on the surface of the Earth and the events that initiate these processes traditionally have been characterized in two broad categories: episodic and cyclic. Classic geological thinking mainly put emphasis on cyclic behavior. However, many of the dominant processes recorded by depositional and erosional features result from episodic events that are extremely energetic. Discussion of extreme episodic events affecting the coastal environment typically results in a list of phenomena such as floods, storms, earthquakes, submarine slides and tsunami. Because they can be treated discretely, they are the preferred target of modelers and theoreticians. However, for these efforts to be successful in interpreting the history of past events and predicting future events, not only the physics but also the duration, recurrence and sedimentary signature of the respective event need to be better understood (Srinivasalu et al., 2006)

Tsunami is a sudden non-meteorologically induced impulse in water regardless of size. These waves are formed by sudden displacement of the sea bottom surface due to submarine tectonic activity particular during to earth quakes. Tsunami can also occur due to volcanic eruption, displacement of the seafloor, landslides near the coast, meteor impact and man made nuclear explosions in the sea. The velocity of the tsunami varies and depends on many parameters such as bathymetry, height of the originating wave, initial pressure changes in the sea, etc. and can travel with velocity of more than 1000 km/hr (Harinarayana and Hirata, 2005). The wave length is large; measuring several hundred kilometres but the wave height is often around one metre only. Since the velocity is proportional to the depth of the water column, the velocity reduces to a few tens of kilometres as the tsunami approaches the coast. However, the wave height increases and may reach even upto 100 m in extreme cases (Tinti, 1991, IOC Report, 2002). As a result the tsunami strikes the coast with massive force inundating large coastal tracts. The effect is colossal in islands with low relief.

The tsunami wave generated can divide at the shore or break and some times appear as flooding with water rushing inside the land more violently and with great force towards a river or stream course. In several cases, when the tsunami arrives, the water level in the sea may drop significantly and the waters receding several hundred metres comes back with great speed faster than a man can run (Bryant, 2001)

Tsunami is common in the Pacific Ocean and frequently originates in the belt comprising the Aleutian Islands, Kamchatka Peninsula, Japan, Chilean Coast, Alaska. The Indian Ocean was considered relatively free of this catastrophic hazard although Valdia (1987) opines that tsunami is possible on a lesser scale in the Bay of Bengal if massive earthquake occurred in the Andaman trench, no strategy to combat the hazard was existed in the South Asian countries. The need for early warning system in the north Indian Ocean was not taken seriously even though Geoscience Australia stressed the need for the establishment of an Indian Ocean warning system in the AUSGEO News 75 September 2004 edition. In a NASA and ISRO Conference on disasters held in June, 2004 in Bangalore Roger Bilham from University of Colorado in his presentation "Quantifying Tsunami Risk" warned of the possibility of a tsunami originating in the Indian Ocean. None expected that these predictions are going to be true until the tsunami struck the region with a destructive force. It is only after 26th December 2004, the scientific community in India realised the need for assessing the vulnerability of Indian coast for tsunamigenic damage.

Earthquakes of such magnitude have never occurred in the Northern Indian Ocean though the Andaman-Sunda trench is an active tectonic belt. This is evident from Table 1. that shows the details of the past earthquakes with a magnitude of 8.5 or greater. From the data we can infer that the 26th December, 2004 earthquake is the world's largest earthquake in the last 40 years since the Prince William Sound Earthquake in 1964 in Alaska and is the largest in the history of Indian Ocean.

2.1 Past tsunamis in Bay of Bengal

Tsunamis are rare in the Indian Ocean but not new. Unlike the Pacific region where many damaging tsunamis occurred, the occurrence of large tsunami in Bay of Bengal is relatively infrequent. During the last 10 years in the Pacific region four major tsunamis in Nicaragua – 1991; Flores, Indonesia – 1992; Okushiri Island, Japan– 1993; and Papua New Guinea -1998 (Dawson et al., 2004) have occurred. In Bay of Bengal, during 1881-2004, 4 tsunamis have been recorded, besides the 26th December 2004 tsunami. The Previous tsunamis in the Bay of Bengal are in 1881,1883, 1907 and 1941 (NOAA compilation). Tsunamis also occurred from Sumatran earthquakes of 1833 and 1861 but before the introduction of harbour tide gauges in most parts of the world. As no scientific data are available they were not recorded.

1. On the morning of 31st December 1881 a submarine earthquake beneath the Andaman Islands having a magnitude of 7.9 generated a tsunami with a maximum crest height of 0.8 m. The 1881 tsunami amplitude attained 1.04 m at Chennai (at low tide) and was caused by 2.7 m of slip on a 150 km by 50 km patch centered on Car Nicobar (Ortiz and Bilham, 2003).
2. The waves from the Krakatoa eruption of 1883 caused measured maximum amplitude of 56 cm (Walker, 1884; Ortiz and Bilham, 2003), contrary to recent assertions of larger amplitudes claimed by several authorities.
3. The 1907 earthquake (Mw=7.6) have ruptured the region near Southwest Sumatra and 400 people were dead. The maximum tsunami run up was 2.5 m. (Soloviev, and Go, 1974).
4. The 1941 earthquake (Mw=7.7) occurred just before the Japanese occupation of the Andaman Islands and appears to have ruptured the region near South Andaman Island. No tsunami records have survived for the 1941 earthquake, and despite an unattributed claim of 3000 dead (Murty and Rafiq, 1991). Were the earthquake Mw=7.7, the tsunami amplitude would have been less than 1 m. These data indicate that the active margin of Sumatra and Andaman region is characterized by strong seismic and volcanic events which have generated tsunamis in the past. These tsunamis had effect on Tamil Nadu Coast and should have deposited sediments related to these events in this region.

Tsunami is not a one-time phenomenon and occurred so many times in history. The impact of Tsunami is going to have the numerous affect on the coastal ecosystem. So it is necessary to keep track of tsunami impacts.

The greatest number of publications (Fig. 1) related to natural hazards, falls under the discipline of Geology (n= 504), followed by Seismology, Tsunami Science, Engineering and Wave modeling. Geologic publications (n= 516) were subdivided into nine topical areas. The most frequently published topic, in the discipline of Geology, is geological field surveys of tsunami and paleo-tsunamis (n= 295) followed by composite topic of landslides and turbidity currents (n= 136). Within the Engineering Discipline there are 361 publications (Fig. 2). The majority of these publications (n=212) focus on modeling studies (Keating, 2006).

2.2 Previous literature on Tsunami

As tsunami is a potential hazard to the costal communities, considerable work has been carried out on tsunami generating mechanisms, the origin, propagation and deformation of the tsunami waves, or the physics of tsunami runup and inundation (Scheffers and Kelletat, 2003). Sedimentology of tsunami deposits is an emerging field of research (Dawson, 1999). According to Keating et al. (2004), tsunami deposits can be classified into three primary categories viz: large clasts, coarse and fine sediments and other obscure deposits such as wash-over fans. Return time of tsunami is attempted based on event history and sedimentological studies on beach deposits. Distinguishing the characteristics of storm deposits and tsunami deposits is also investigated (Goff et al., 2004). Studies on geomorphic alterations due to tsunami are limited. After detailed review Scheffers and Kelletat (2003) concludes that studies on geomorphic alterations are restricted to four regions described in about 15 articles (Bryant, 2001; Bryant and Young, 1996; Bryant et al., 1996, 1997; Young and Bryant, 1992, 1993; Kelletat and Schellmann, 2002; Southern Caribbean: Scheffers, 2002a, b). While most of the papers discuss the changes consequent to deposition, shoreline changes due to erosion are restricted due to lack of pre-tsunami data. Destruction of roads, buildings and other man made structures is used as evidence for the erosional impact of tsunami (Keating et al., 2004)

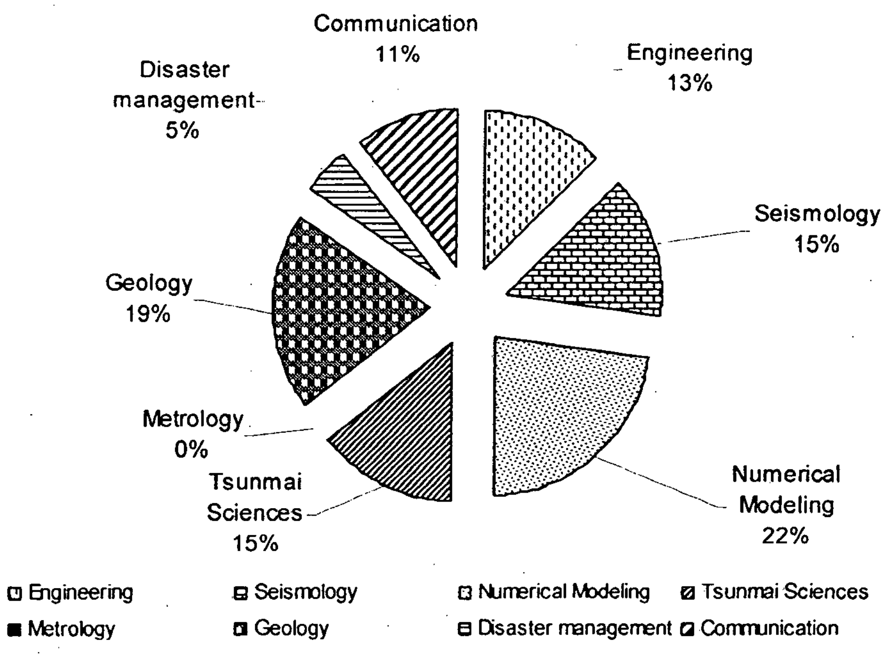
Several investigations attempt to describe and estimate the role of tsunami impacts on the Pleistocene and Holocene coastal development. According to Bryant (2001), the effects of tsunami on coastal forming processes are in general rather limited, but occasionally they may have played a major role. Bryant et al,. (1996) suggested that extreme Holocene tsunami events have been the dominant factor for the coastal development in south-eastern Australia, were primarily responsible for the formation of barrier islands, cliffs, canyons, and sculptured bedrock forms. To carve bedrock forms like, e.g. flutes or vortexes, extreme flow velocities are necessary a fact that suggests that tsunami are responsible, as opposed to large storm waves.

Table 2.1 Deadliest Earthquake in World (1990-2005)

Region	Date	Year	Magnitude	Fatalities
Northern Sumatra, Indonesia	28-Mar	2005	8.7	80,361
Off West Coast of Northern Sumatra	**26-Dec**	**2004**	**9**	**283,106**
Hokkaido, Japan Region	25-Sep	2003	8.3	31,000
Central Alaska	3-Nov	2002	7.9	1,000
Near Coast of Peru	23-Jun	2001	8.4	20,023
New Ireland Region, P.N.G.	16-Nov	2000	8	103
Taiwan	20-Sep	1999	7.7	17,118
Balleny Islands Region	25-Mar	1998	8.1	4,000
South of Fiji Islands	14-Oct	1997	7.8	1,572
Near East Coast of Kamchatka	5-Dec		7.8	
Irian Jaya Region Indonesia	17-Feb	1996	8.2	322
Near Coast of Northern Chile	30-Jul	1995	8	5,530
Near Coast of Jalisco Mexico	9-Oct		8	
Kuril Islands	4-Oct	1994	8.3	795
South of Mariana Islands	8-Aug	1993	7.8	9,748
Flores Region, Indonesia	12-Dec	1992	7.8	2,519
Costa Rica	22-Apr	1991	7.6	2,000
Kuril Islands	22-Dec		7.6	
Luzon, Philippine Islands	16-Jul	1990	7.7	50,000

Source: USGS (2005), National Earthquake Information Centre

Fig.2.1 Distribution of publications by scientific disciplines (% of total publication)



(Source: Keating, 2006)

2.3 Studies done in India in Tsunami Perspectives

Tsunami is a catastrophic natural hazard that is uncommon in the Indian Ocean. Hence, no strategy to combat the hazard was existing in the South Asian countries. The reports on tsunami in Indian coast prior to 26th December, 2004 tsunami is limited. There were reports on the tsunami that formed consequent to the explosive volcanism of Karakatoa volcano in 1883 (Choi et al., 2003), 26th June, 1941 tsunami consequent to the earthquake with a magnitude of 8.1 in Andaman Sea and the earthquake 70 km south of Karachi (Gupta, 2005). After the tsunami event several illustrative reports describing the dynamics of the Asian tsunami were posted in the internet. The information include the location and characters of the earthquake that originated the tsunami (USGS, 2004), slip distribution (Yamanaka, 2004), regions affected by the tsunami and the time of striking the coast (OCHA, 2005). Numerical modelling results based on bathymetric data (DCRC, 2005), etc. With the initiative taken by the Indian geoscientific journals like Geological Society of India, Current Science, etc., several reports on tsunami damage appeared in the months of February and March, 2005. Most of the short communications and notes are based on site investigations and comparison of pre-tsunami and post-tsunami satellite images field reports and enumerating the damage to geomorphology and property (Narayana et al., 2005; Vaidyanathan, 2005), changes in groundwater quality (Ballukraya, 2005; Prasad and Raj, 2005), changes in the geochemical characters of nearshore waters (Reddy et al., 2005) and heavy mineral deposition. Various other studies involve the ecological impact of tsunami on Andaman and Nicobar Islands (Ramachandran et al., 2005, Venkataraman et al., 2006). The unusual height of waves during high tides during May 2005 was reported in the Kerala cost (Baba, 2005) whether it is due to changes in near-shore bathymetry due to tsunami is a matter to be investigated. Mahadevan (2005) observes that the tsunami did not affect the northern part of Bay of Bengal as the Bengal fan offered resistance to its travel and similarly their northward movement in the Arabian Sea was prevented by the Indus sediment accumulation.

Thirty papers presented in the Brainstorming session organised by Bharathidasan University were published by Allied Publishers as Tsunami: The Indian context (Ramasamy and Kumanan, 2005). The papers deal with various aspects of tsunami including the triggering mechanism and propogation, runup and inunadation, vulnerability and impacts and mitigation strategies. The papers highlight the damage caused to the Tamil Nadu, Kerala, Andhra Pradesh and Andaman and Nicobar islands.

Few reports based on measurement of inundation and run up in tsunami affected regions which are relevant to the proposed project were also published (Chadha et al., 2005; Narayan et al., 2005; Ram Mohan, 2005; Jayakumar et al., 2005). Chadha et al., (2005) reported the tsunami run-ups estimated in 11 locations from Pulicat to Vedaranyam. Their run up estimates range from 2.5 to 5.2 m. and inundation varied between 160 to 800 m. The also estimated the direction of tsunami and found it to be oblique to the coastline and varied by 30 to 40° from shore normal. Narayanan et al., (2005) estimated the run up and inundation in 40 locations from Chennai to Colachal in Tamil Nadu and according to them the run up ranges from 1 to 12 m and inundation varies between 20 to 7000m. The minimum run up and inundation is recorded in the costal region of Palk Strait which suffered less damage as it was protected by Sri Lanka. The highest inundation according to them was in Velankanni wherein nearly 1000 people have lost their life. The high run up in Nagapattinam district according to them was due to the bathymetry of continental shelf and interference of direct wave and waves deflected by Sri Lanka.

Ram Mohan (2005) made a field survey and reported run up ranging from 3 to 8 m in the coastal stretch from Pulicat to Vedaranyam based on observation in 41 locations. The inundation according to him is ranges from 50 to 2000 m. Ramanamurthy et al., (2005) estimated the run up and inundation in Tamil Nadu and Andaman and Nicobar islands and presented a comprehensive report including the rise of sea level by 1.5 m which continued even after a week from the day of tsunami.

Jayakumar et al., (2005) found that the dune ridges protected the coast and wherever there are openings in the dunes, the tsunami inundation was higher. They attribute the flat topography for high inundation in Nagapattinam a point that was observed by all. They opine that the waves converge and increase run up in concave coasts and divergence in convex coasts lead to decrease in run up.

The research work carried out by Szczuinski et al (2005) revealed the various aspects of soil and water contamination in coastal zone of Thailand after Tsunami and had shown that tsunamigenic sediments are poorly sorted from coarse silts to medium sands and reported elevated contents of salts in sediment. Anil Kumar et al., (2006) studied the post-tsunami oceanographic conditions in southern Arabian Sea and Bay of Bengal. Several studies on the impact of tsunami on Sri lanka was also carried out, such as on terrestrial ecosystems of Yala National Park, Sri Lanka (Prithiviraj et al., 2006).

More recently, in 2006, a comprehensive report on "Tsunami-Causes, Effects, Remedial Measures, Pre and Post Tsunami Disaster Management –A Geoscientific Perspective" was published by Department of Science and Technology, New Delhi, Govt. Of India, which was involve scientific organizations to put emphasis on understanding of scientific issues related to areas in tsunami affected states of Tamil Nadu, Andhra Pradesh, Kerala and Andaman and Nicobar Islands covering theme on inundation mapping (Subramanian et al., Kumar et al.), coastal geomorphology (Hussain et al.), surface and groundwater quality (Elango et al.) and characterization of tsunami sediments (Srinivasalu et al., Ramesh et al., Hussain et al.).

2.4 Research Status at Pichavaram Mangroves

A substantial work has been carried out on the changes in the ecological quality due to decrease in freshwater input, pollution, increase in human disturbances and other anthropogenic activities, which causes degradation of mangroves faunal biodiversity by 59.1 %. Because of these problems, light intensity has increased by 42% and salinity by 64% (Kathiresan, 2002, Kavi Kumar, 2003, Krishnamoorthy et al., 2003). The Pichavaram mangrove has also been studied in detail for its floral and faunal communities and bacterial abundance (Blasco et al. 1975, Mittene and Sharma, 1975, Govindaswamy and Kannan, 1991, Jagdeep et al., 1993, Kathiresan et al., 1994). The geochemistry of the Pichavaram mangroves and adjoining estuaries was studied in detail to assess the weathering activity and material influx to the mangrove system (Seralathan and Seetharamaswamy, 1987, Subramanian et al., 1989, Purvaja and Ramesh 1998, Ramanathan et al., 1999). Ramanathan et al., (1993) was first reported the

^{13}C values in the Cauvery estuary at selected locations and explains the ^{13}C were enriched in the lower reaches than the upper reaches and the depleted signature values reflect the dominance of the terrestrial river derived material to the estuarine system. Flux of the green house gas, methane (CH_4), has been quantified by Purvaja and Ramesh (2000).They reported that CH_4 emission from the polluted zone of the mangrove is 369.6 mg m^{-2} d^{-1} and from un-polluted zone is 117.12 mg m^{-2} d^{-1} and assessed the factors responsible for the spatial variability in both natural and human impacted mangrove zones in the Pichavaram mangrove along with the tidal impact. Prasad and Ramanathan (2005) had studied the seasonal variations in nutrients status of water of the mangrove system. Khan et al.,(2004) had explained the industrial pollution load in the Pichavaram are with respect to functioning 43-odd chemical and pharmaceutical set up by SIPCOT. More recently, Alongi et al., (2005) studied human-induced disturbance on benthic microbial metabolism and had concluded that vertical alteration of soil characteristics and biogeochemistry shifts the nutrient cycling within trees and microbes to a disequilibrium state, partly explaining why mangroves are stunted in this declining forests. As a part of an integrated biogeochemical study of the mangrove environment, the distribution and enrichment of the rare earth elements (REE) was attempted for the first time to understand the biogeochemical processes taking place in this hypersaline coastal wetland (Prasad and Ramanathan 2006). Prasad and Ramanathan (2006) had also traced food web dynamics in this mangroves using Carbon and nitrogen stable isotope.

2.5 Studies Carried out Pichavaram Mangroves in Tsunami Perspectives

Srelathan et al., (2006) collected surfacial sediments and core samples from different locations after tsunami from Cuddalore to Pichavaram mangrove area and compared the variations with pre tsunami sediments collected in the same location to decipher the impact of tsunamigenic sediments from pre and post tsunami sediments. They had observed that tsunamigenic sediments are coarse than pre and post tsunami sediments with a narrow range of mean size due to rapid sedimenatation by tsunami waves. They had described the standard values, kurtosis and skewness values for the sediments. They further concluded that tsunamigenic sediments contain abundant heavy minerals than the pre-tsunami sediments.

2.6 Backdrop of the present study

Based on the extensive review, we can infer that there is few comprehensive/systematic study available on comparison of pre and post tsunami biogeochemical changes including sediments from the Pichavaram mangrove area. The study covers all aspect biogeochemical changes such as water quality (physiochemical parameters), grain size analysis of sediment and its control over nutrient uptake and release etc. The present study also includes the nutrient (micronutrient as well as macronutrients), phosphorus speciation heavy metals and their speciation in surface and core sediments. So, overall this study is a contribution to a better understanding of the effects of tsunami on mangroves and its coastlines. The observations of modern tsunami sediments will ultimately help to improve the identification and interpretation of palaeotsunamis in the geologic record in near future.

Chapter 3

Materials & Methods

3.1 Study Area

The study site, the Pichavaram mangrove (Lat 11° 23' and Long 79° 47'), is located between the Vellar and Coleroon estuaries and has direct opening to the Bay of Bengal at Chinnavaikkal (Fig. 3.1 and 3.2). The area of the mangrove forest is 1100 ha, 50% covered by forest, 40% by water ways and rest filled by mud and sand flats (Krishnamurthy and Jayaseelan, 1983). It has 51 islets ranging in size from 10 m^2 - 20 km^2 separated by intricate waterways, that connects the Vellar and Coleroon estuaries.

The southern part of the mangrove forest dominated by mangrove vegetation, while northern part near the Vellar estuary is dominated by mud flats. The Pichavaram mangrove influenced by mixing of the three types of waters (Kathiresan 2000).

1. Neritic water from the adjacent Bay of Bengal through a mouth, Chinnavaikkal.
2. Brackish water from the Vellar and Coleroon estuaries and,
3. Fresh water from the irrigation canal (Khan Sahib Canal) as well as main channel of the Coleroon river.

The tides are semi-diurnal varying in amplitude from about 0.1 to 1 mtr in different regions during different seasons, reaching maximum during monsoon and postmonsoon and minimum during summer. The rise and fall of the tidal waters is through a direct connection with the sea at Chinnavaikkal mouth and also through the two different estuaries, the Vellar and the Coleroon (Fig. 3.1). The depth of the water ways range from about 0.3 to 3 m.

3.1.1 Geology

Since the Pichavaram mangrove ecosystem is lying between the rivers Vellar and Coleroon, therefore alluvium is dominant in the western part and fluvial marine and beach sand cover eastern part of the mangrove. Geomorphology of the area is major area covered by floodplain, sedimentary plain and beach sand. Major part of the area falls under nearly level sloping category. The soil group of the area is Hydrological soil group

`C' (USDA) low infiltration and moderate runoff potential found 50% area. The soil group `B' with moderate runoff is covering about 45% areas. The remaining 5% area is occupied by soil group `A' with high infiltration low runoff potential.

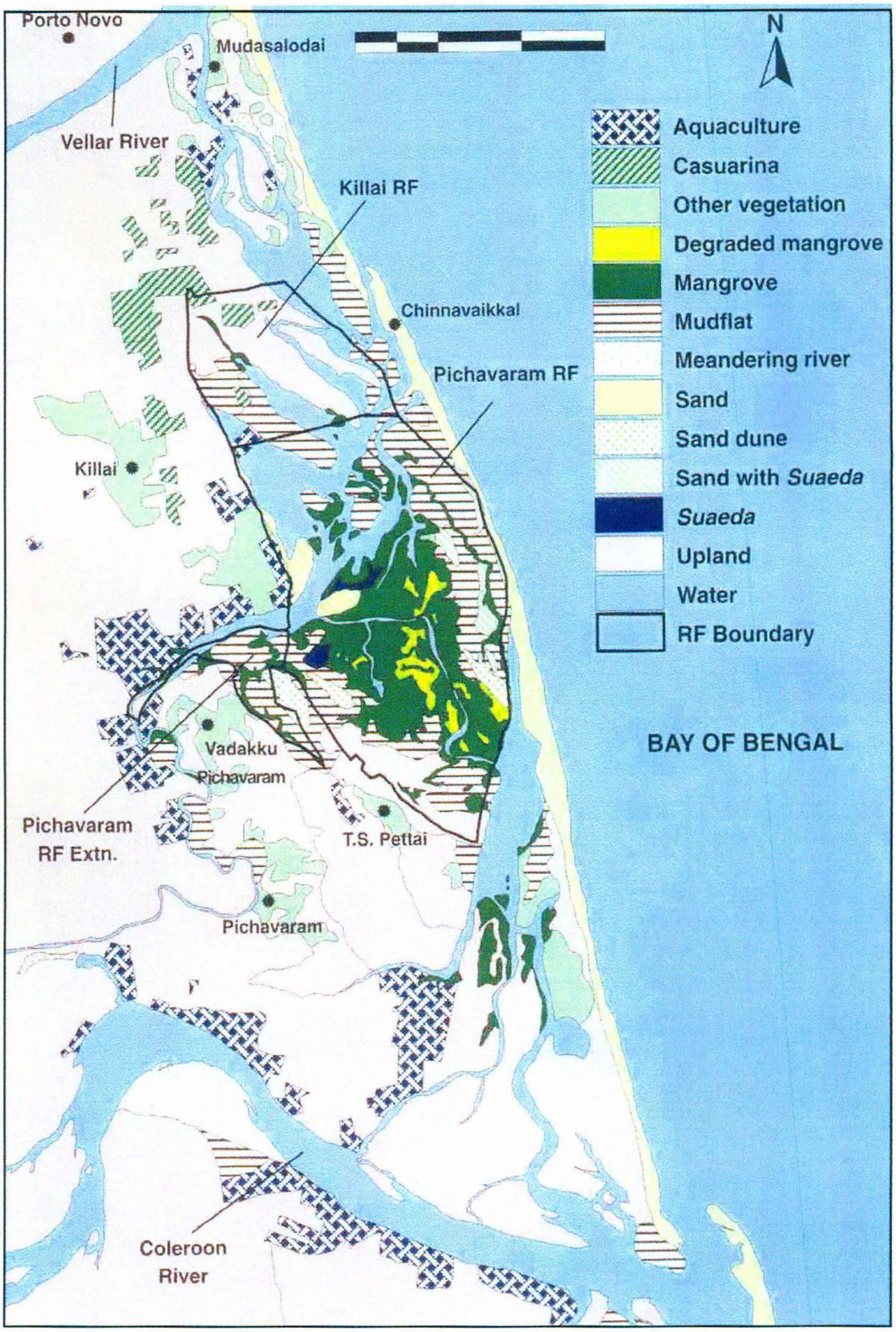


Figure 3.1 Map of Study area
(source: Selvam et al., 2003)

3.1.2 Climatic Conditions

The weather condition in the Pichavaram mangrove area is typical tropical climate. For the sake of convenience, the whole year is divided into 4 seasons: Post-monsoon (January–March), summer (April – June), Pre-monsoon (July – September) and two monsoons (south-west monsoon from June to July and north-east Monsoon October to January). Maximum and minimum temperature was ranged from 29 – 36°C and 18.2 – 25°C respectively. The wide range of temperature fluctuations drives rapid changes in the daily and monthly mean humidity in the atmosphere along with the wind speed which may be one of the main factors controls the nutrient chemistry in this area.

There is a wide fluctuation in total precipitation. Annual rainfall was 1463.9 ± 329.9 mm during 1998 – 99, and the number of rainy days was 53 ± 8.7 (Kathiresan, 2000).

3.1.3 Flora and Fauna

The Pichavaram mangrove is one of the best example for best flora and fauna , both micro and macro. This mangrove forest has 13 species of true mangrove species (Kathiresan and Ramanathan 1997) and by degree of abundance *Avicennia and Rhizophora* are the most common and dominant species. The fertile status of the mangrove soils is controlled by the rich microbial flora in the mangrove sediments.

The mangrove ecosystem harbours both invertebrate and vertebrates. Belonging to polychaetes, bivalves, gastropods, tanaids, isopods, amphipods, cirripedes, crabs, shrimps and hermit crabs (Kathiresan 2000).

3.2 Sampling Location

12 Water samples and 12 surfacial sediments samples were collected from different locations covering the entire Pichavaram mangrove (Fig. 3.2) and adjoining estuarine complex during the month of January 2005 in order to understand the impact of Tsunami on nutrient behavior. Three cores were collected from the area .in order to get the broader picture of the interaction of various components (viz. Tsunami, Anthropogenic input, matural impact etc.) and their interaction with the nutrient dynamics, the sampling location were carefully decided for study and were fixed by using GPS (Table 3.1).

3.2.1 Sample collection and preservation

Water samples were collected in pre washed bottles of 300 ml and 150ml for nutrient and heavy metal analysis respectively. Smaller part was filter using Whattman 0.45µ

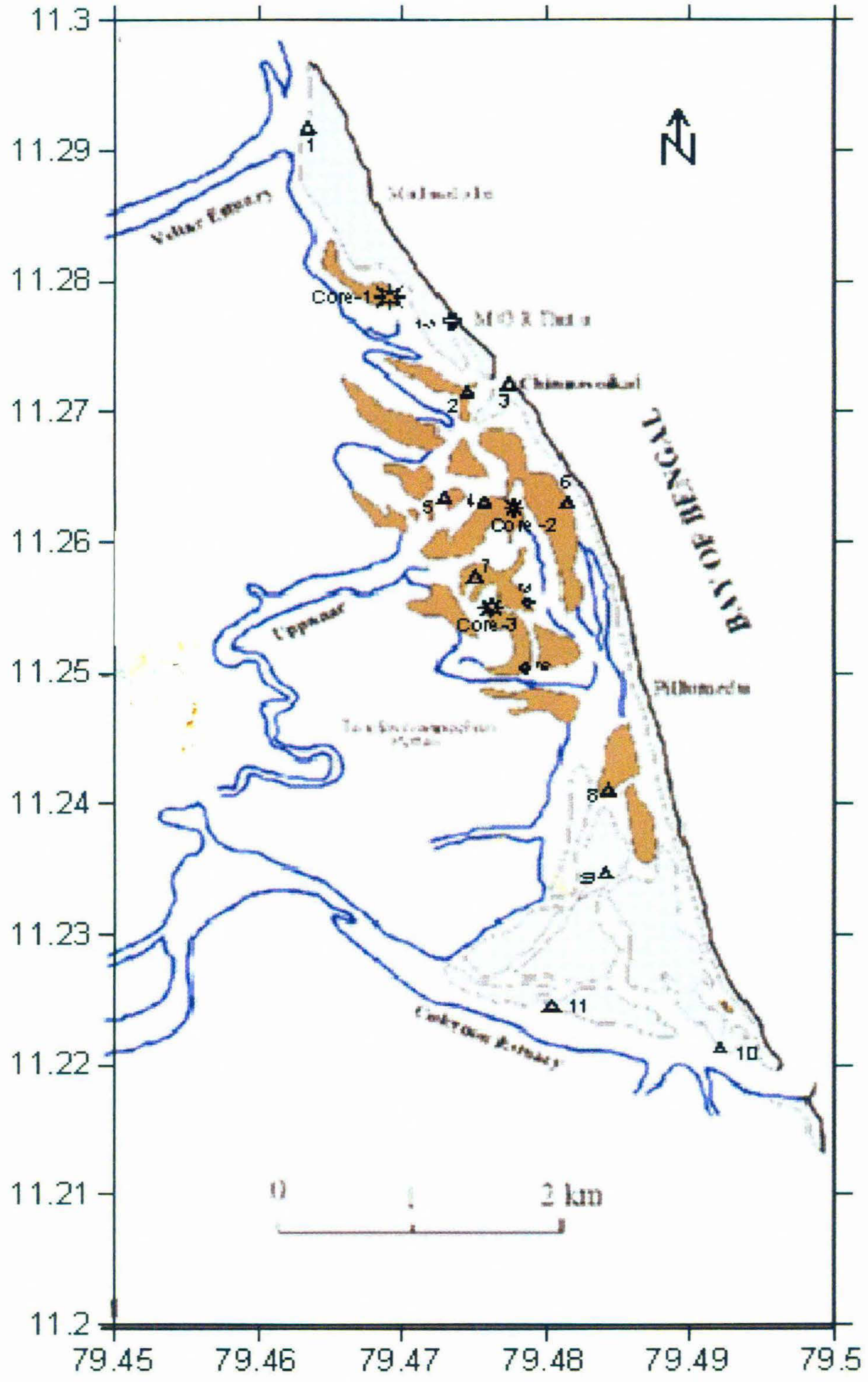


Fig. 3.2 Map of Study area showing sampling locations

Table No 3.1 Sampling locations in the Pichavaram Estuarine complex

Sample No	Sample Id.	LOCATION	Longitude	Latitude
1	1	Vellar	79.7710	11.4977
2	1A	MGR Tittu	79.7846	11.4630
3	2	Chinnavaikkal 1	79.7892	11.4377
4	3	Chinnavaikkal 2	79.7916	11.4531
5	4	Mangrove Forest 1	79.7949	11.4662
6	6	Mangrove Forest 2	79.8037	11.4391
7	7	Mangrove Forest 3	79.7894	11.4533
8	7A	Mangrove Forest 4	79.7879	11.4257
9	7B	Mangrove Forest 5	79.7917	11.4249
10	8	Mangrove Forest 6	79.8053	11.4053
11	9	Coleroon 1	79.8079	11.3898
12	10	Coleroon 2	79.8201	11.3688
13	11	Coleroon 3	79.8255	11.3517
1	CORE 1	Vellar	79.7927	11.4252
2	CORE 2	Mangrove Forest	79.7894	11.4054
3	CORE 3	Mangrove Forest	79.7889	11.4688

Legend

△ -Surface sediments
✲ - Core sediments

cellulose nitrate filter paper and was fixed using HNO_3 for heavy metal analysis .Second fraction was kept for dissolved nutrient analysis. Sediments samples (1 kg each) were collected in the polyethylene bags. Three cores were collected by using a stainless steel corer of ID 7 cm. The core was cut at 5 cm interval and the segments were transferred into polythene zip bags. Collected samples were stored in ice chest in the field and were immediately transferred to laboratory for further analysis. In the laboratory, the samples were kept at 4° C. pH, EC, TDS, and ORP (by using Thermo Orion Probes) and DIC (by titrimetric method) of the water samples were measured in the field.

3.3. Analytical procedure

3.3.1 Analysis of water samples

3.3.1.1 Anions analyzed

Bicarbonate

The bicarbonate content was determined following the potentiometric titration method (APHA,1998). Bicarbonate standards ranging from 100-1000ppm were prepared from $NaHCO_3$. 50 ml sample and a series of bicarbonate standards were titrated against 0.02N HCl. The end point was noted at pH 4.5. A standard graph was plotted between bicarbonate standards and volume of the acid consumed. The reading of samples was noted down from the graph.

Chloride

Chloride content was determined by titration methodAs prescribed by APHA(1998) . The samples pH range was adjusted between 7 to 10 with H_2SO_4 or NaOH. 1ml of K_2CrO_4 indicator solution was added in samples.Samples were titrated with standard $AgNO_3$ titrant to a pinkish yellow end point. Chloride was calculated using equation

$$\text{Cl (mg/l)} = (A-B) \times N \times 35{,}450/\text{ml sample where}$$

A = ml titration for sample
B = ml titration for blank
N= normality of $AgNO_3$

Nitrate

Nitrate in the mangrove water was measured by Brucine–MBTH Method (Nagaraja et al., 2003). 10 ml of the sample was taken in 100 ml conical flask and 100 ml of 14.4 mol/L H_2SO_4 was added followed by addition of 5 ml Brucine – MBTH reagent mixture (1 g of brucine sulphate + 0.5 g 3-Methyl 2-Benzothiazolinone hydrazone hydrochloride (MBTH) in hot water, cooled and made up to 100 ml) with swirling. The solution was allowed to stand for 10 min for the development of the yellow colour. When the solution was made up to the mark with water, the colour was turned into violet instantaneously. The absorbance was measured at 560 nm against the blank.

Dissolved Inorganic Phosphate (DIP)

DIP was measured in terms of phosphate (PO_4) in the mangrove waters. Phosphate is measured by Ascorbic Acid Reduction Method (Edwards et al., 1965; Murphy and Riley 1962). To 50 ml of sample taken in the Erlenmeyer flask, 8 ml of combined reagent was added (mix 50 ml 5N H_2SO_4 (dilute 70 ml conc. H_2SO_4 in 500 ml distilled water), 5 ml Potassium antimonyl tartarate (dissolve 1.3715 g $K(SbO)C_4H_4O_6.\frac{1}{2}H_2O$ in 400 ml distilled water and dilute to volume), 15 ml ammonium molybdate solution (dissolve 20g $(NH_4)_6Mo_7O_{24}.4H_2O$ in 500 ml distilled water) and 30 ml ascorbic acid solution (dissolve 1.76 g ascorbic acid in 100 ml distilled water) and mix thoroughly. Between 10 – 30 min, blue colour was developed and absorbance of colour was measured at 880 nm.

Sulfate

Buffer solution –30 g $MgCl_2$, 5g CH_3COONa, 1g KNO_3 and 20 ml CH_3COOH was mixed thoroughly. Standard solutions were prepared by dissolving 0.1479 g of Na_2SO_4 in 1 liter water (100ppm). Other standard were prepared by Stock solution. 5ml buffer solution, $BaCl_2$ in 25 ml water sample and Optical density was measured by spectrophotometer (JENWAY 6505, UV/VIS) at 420-nm wavelength.

3.3.1.2 Cations analyzed

Ammonium

Ammonium was determined colorimetrically using the method prescribed by Solórzano, 1969, and Presley, 1971. 1 ml Samples (and standards) were taken into scintillation vial. 1 ml of Phenol solution (4 g phenol/ 500 ml of ethanol) was added. 1ml of Nitroprusside solution (0.75 gm nitroprusside/ L) and 2 ml of oxidizing solution (4 ml sodium hypochlorite (NaOCl, 5%)/ 100ml of alkaline solution prepared by dissolving 15 g trisodium citrate and 0.8 g NaOH/ L distilled water . Color was allowed to develop for 4 to 6 hours and absorbance was read at 640 nm.

Sodium, Potassium, Calcium

These cations were analyzed using Flame-Photometer.

Heavy metals

Selected heavy metals were analyzed using Atomic Absorbtion Spectroscope (SHIMADZU)

3.3.2 Analysis of Sediments

3.3.2.1 Grain size analysis

Sediment Textural Analysis

The mechanical analysis normally begins with sieve procedures, the separation of sediment samples into different size classes i.e.> 125 μm, 125-250 μm, 63-125μm, <63 μm from homogeneous sediment samples. Further separation of <63μm samples into 50, 30, 20, 10, 5, < 5μm were carried by Atterberg sedimentation cylinders with dry and organic content free samples in order to minimize the possibilities of flocculation of clay minerals.

Atterberg Sedimentation Cylinders

It is a 35 cm long cylinder having 5 cm diameter and is provided with a siphon at 3 to 4 cm above the base. Cylinders were graduated in centimeter with the zero mark coinciding with the siphoning layer of the liquid. The siphon tube was connected to a rubber (latex) tube which was provided with a pirch cork. Cylinder at mouth was provided with a glass. A homogenized suspension in water was prepared from samples. Homogenisation was carried out with the aid of mechanical stirring. The strength of the suspension was maintained. The suspension was transferred to Atterberg sedimentation Cylinders (Griffiths, 1967) and again was shaken before keeping for size separation .The different fractions were evaporated at 600° C in a porcelain dish on hot plate.

Principle of size separation by Atterberg sedimentation Cylinder

Stock's law (Griffiths, 1967) governs the size separation of sediments which states the law of settling velocity:

$$V=2\, r^2 g\, (d_1-d_2)/\,/9\, \eta$$

where V=velocity of settling,
d_1=density of particles,
d_2=density of fluid medium,

g=acceleration due to gravity
η=viscosity of fluid
r= radius of particles

For time given diameter of particle is T=h/V where h= fall height of suspended column
V=Settling velocity.

3.3.2.2 Analysis of major and minor elements:

Fine ground homogenized sediments were taken in the beaker and heated with 30% (v/v) H_2O_2 (Jackson, 1973) for removal of organic matter. The treatment was repeated until the CO_2 emission stopped. Analyses of Major and Minor elements were carried out by the two solution methods (Shapiro, 1975). Solution "A" was used for silica, Alumina and Phosphorus analysis and solution "B" was used for metal analysis.

Prepartion of Solution A

0.025 gm of finely powdered sediment was taken in 50ml Nickel crucible and 3-4 pellets of NaOH were added to it. The crucible was gently heated on a furnace in order to mix sediment melt pellets, and then the crucible was constantly heated to dull redness for 30 mts. Then the crucible was allowed to cool down to room temperature. 10 ml of distilled water was added in the crucible and kept overnight. The solution was transferred to 250 ml volumetric flasks. 5ml of (1:1) HCl and 25ml of water was added. This solution was boiled till it was clear and the total volume was made up to 250 ml by adding distilled water.

Preparation of Solution 'B'

0.1gm of finely ground sample was transferred to the Teflon crucible and 2ml of Aqua- regia (HNO_3 and HCl ratio 1:3) and 5ml HF were added to each crucible, these were then sealed in metallic cases. The crucible was heated for 1.5 hrs at 100°C and then allowed to cool down to room temperature. 5.6gm of Boric acid crystal (H_3BO_3) was dissolved in 20 ml distilled water and then added to the bomb content that was made up to 100ml. The solution was transferred to polypropylene bottles for storage. The sample was left undisturbed overnight to allow the formation and setting of borosilicate from the solution. The gelatinous precipitate is separated by centrifugation followed by filtration using Whattman 0.45µ cellulose nitrate filter paper.

Silica Analysis:

0.8ml of solution 'A', Standard solution (Canadian soil standard i.e.SO1, SO2, SO3, SO4) and reagent blank were transferred to 50ml Teflon beaker. 20ml of distilled water was added to each beaker. 0.2ml of Ammonium molybdate solution (prepared by dissolving 1.875 gm. ammonium molybdate in 19ml distilled water and adding 6ml 20% (v/v) H_2SO_4) was added and kept for 10 minutes. 0.4ml of 10 %(w/v) Tartaric acid was added by swirling the beaker. 0.1ml of reducing reagent (prepared by dissolving 0.07gm sodium sulphite in 1.0ml-distilled water and then 0.015gm 1-amino-2-naphthol-4-sulphonic acid was added and stirred well until dissolved. 9ml of 10 %(w/v) sodium bisulphite solution was added to it and mixed well) was added and samples properly stirred and kept for 30 minutes. Optical density was measured at 650 nm spectrophotometer.

Alumina Analysis:

15 ml of solution 'A' (Sample, Standared and Blank) was taken in 100 ml volumetric flasks. 2 ml calcium chloride solution (prepared by dissolving 7gm $CaCO_3$, 100ml of water, and 15ml of conc. HCl and diluted to 500ml) was added. 1 ml of Hydroxylamine hydrochloride solution (prepared by dissolving 5gm of hydroxylamine hydrochloride in 50ml) was added by swirling the flask. 1 ml of potassium ferricyanide (0.75%) was added to each flask and mixed. 2 ml of Thioglycolic acid solution (4%) was added and kept for 5 mts. 10ml of Buffer solution (prepared by dissolving 100gm of sodium acetate in water and adding 30gm glacial acetic acid and diluted to 500ml) was added and kept 10mts. 10ml of Alizarin Red-Solution (0.05%) was added to each flask and the volume was diluted to 100ml by adding distilled water. The samples were properly stirred and kept for 50 minutes. The absorbance was measured at 470 nm

Phosphate Analysis:

Total phosphorus in sediment was determined by Ascorbic acid method (APHA, 1998). Phosphate Standard solution ranging from 0.1 to 3 ppm was prepared using KH_2PO_4. 40 ml of each sample and standards solution was pipetted out in 50 ml volumetric flask and 5ml of Ammonium Antimony solution (prepared by dissolving 4.8 gm ammonium molybdate and 0.1 gm potassium antimony tartarate in 400ml 4N H_2SO_4 and making the total volume to 500 ml with the same acid) and 2 ml of ascorbic acid solution (2 % w/v) was added and mixed well. The mixture was diluted to 50 ml and optical density was measured at 650 nm using spectrophotometer . A graph was plotted between concentrations of the standards and optical density and sample concentrations were obtained from this graph.

Carbon and Sulfur

Sediments were made free of halogens by washing repeatedly with distilled water. Sediments were taken in the beaker and boiled with 30% (v/v) H_2O_2 (Jackson 1973) for removal of organic matter. The treatment was repeated until the emission of CO_2 stopped. Total Carbon and Total Sulfur was analyzed using ELTRA (CS 1000) Carbon Sulfur Analyser. Untreated samples were used for determining Total Carbon and total sulfur whereas the peroxide treated sample was used to measure inorganic carbon. Organic carbon is given by the difference (OC= TC-IC) The measuring method is based on the principle of sample combustion and analysis of gases given off through infrared absorption. Between 2.5 – 4.5 mg of sample was taken in a ceramic boat, and pushed into the silicon carbide furnace set at a temperature of 1100°C. The combustion occurs in presence of oxygen supplied and the carbon present in the samples is converted to CO_2/SO_2 and is detected by the sensor and recorded as % C or % S

Total Nitrogen

Nitrogen was analysed by Kjeldahl digestion method of Anderson and Ingram (1993). 0.2 gm of finely ground sediment was taken in digestion tube and 4.4 ml of digestion mixture was added to each tube. This was digested at 360°C until the solution became colorless. The solution was allowed to cool down to room temperature. 50 ml of distilled water was added in each tube and stirred. The final volume was made up to 100 ml. by adding distilled water. The clear solution was used for analysis. Digestion mixture was prepared by dissolving 0.42 gm Selenium powder and 14 mg Lithium Sulphate in 350 ml and 30% (v/v) H_2O_2 and mixed. In this mixture, 420 ml H_2SO_4 was added carefully while cooling in an ice bath. The digestion mixture was kept at 4°C for further use. Nitrogen was determined by steam distillation. Free ammonia was liberated from the solution by steam distillation in the presence of excess alkali. The distillate was collected in a receiver containing excess boric acid indicator and nitrogen was determined by acid titration. Distillation process was done by transferring 10 ml of aliquot to reaction chamber and adding 5 ml alkali mixture and starting distillation immediately. About 25 ml of distillate was collected in 5 ml Boric Acid-indicator solution. The distillate was titrated against N/140 HCl to a grey end point using micro-burette. The Kjeldahl Nitrogen was calculated using the following equation:

$$\%N = (a-b) * N \text{ of HCl} * 1.4 * V/(v * s)$$

where 'a' is ml. of HCI used against sample,
'b' ml. of HCI used against blank,
'V' ml. of total digest titrated,
'v' ml. of digest distilled and
's' weight of sediment taken.

Alkali solution was prepared by dissolving 500 gm NaOH and 25 gm Sodium thiosulphate in water and final volume was made up to 1000 ml with distilled water. Boric acid-indicator solution was prepared by Okalebo et al., (1993) method. 0.3 gm Bromocerol green and 0.165 gm methyl red were dissolved in 500 ml of 95% ethanol to make the Indicator Mixture. 20 gm Boric acid was dissolved in 700 ml distilled water and cooled and 200 ml of 95% ethanol was added. 20 ml of mixed indicator was added to it and mixed well by shaking. 0.05 N NaOH was added to it until 1 ml of indicator with 1 ml distilled water changed color from pink to pale green. The solution was then made unto 100 ml.

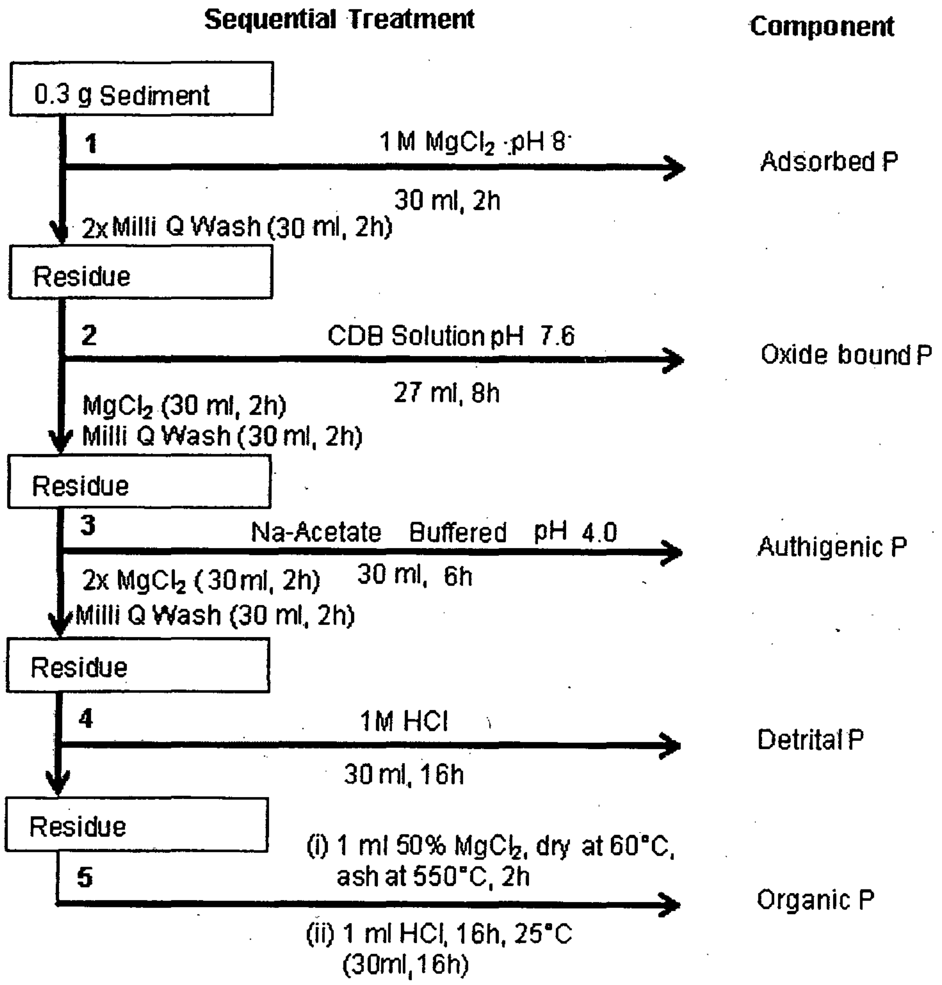
Metals

Heavy metals were analyzed by using Atomic Absorption Spectroscope Shimadzu-AA-6800.

3.3.2.3 Phosphorus speciation

SEDEX sequential extraction procedure (Ruttenberg, 1992) has been adopted to study the P biogeochemistry of the Pichavaram mangrove sediments. 0.3 g of the fine ground sample was taken in pre-washed 100 ml conical flask. During each reaction, as shown in Fig. 3.3, the solution was transferred to 50 ml polyethylene centrifuge tube and was centrifuged at 4500 rpm for 12 min by REMI Centrifuge and supernatants were transferred to acid cleaned polyethylene collection bottles. The collected supernatant was analyses as SRP (except for the second fraction) by methods as described earlier in section 3.3.1

Figure 3.3 Sequential Extraction of Phosphorus in sediments



CDB is combined citrate-diathianite-bicarbonate solution

(Ruttenberg, 1992)

3.3.2.4 Metal Speciation

The following five-fraction (step) SE procedure by Tessier et al., (1979) was adopted for the determination of the trace metals speciation:

1. Exchangeable (adsorbed and exchanged),
2. Bound to carbonates,
3. Bound to iron and manganese oxides,
4. Bound to organic matter (humic substances), and
5. Residual (primary and secondary minerals).

Following procedure was followed for sequential extraction of heavy metals from sediment. For 1 gms of the soil, followed steps were followed and after each step the sample was separated through centrifuge at 5000rpm for 40 minutes. The sample was washed with distill water and dried at 40° C for further analysis

Fraction 1: Exchangeable Process: The samples were extracted at room temperature for 1 h with 8mL of magnesium chloride solution (1M $MgCl_2$, pH 7.0) with continuous agitation.

Fraction 2: Bound to Carbonates Process: The residue from fraction 1 was leached at room temperature with 8mL of 1 M NaOAc adjusted to pH5.0 with acetic acid (HOAc). Continuous agitation was maintained, and the time necessary for complete extraction was evaluated based on the 2000 ppm lead carbonate sample prior to experimental trials and was determined to be 3 h.

Fraction 3: Bound to Iron and Manganese Oxides Process: The residue from fraction 2 was extracted with 20mLof 0.04 M $NH_2OH.HCL$ in 25% (v/v) HOAc. This fraction experiment was performed at 96 ± 3 C with occasional agitation for 6 h.

Fraction 4: Bound to Organic Matter: 3 ml of 0.002M HNO_3 along with 5ml of 30%H_2O_2 (pH adjusted at 2 with HNO_3) was added to the residue from fraction 4 and heated to 85±3 C for 2 hrs with occasion agitation. 12 ml of 30% H_2O_2 was added and the heating was continued for another 3 hrs. On cooling 4 ml of Distilled water was added and was shaken for 30 minutes.

Fraction 5 Residual: the sample was extracted as solution B

3.4. Standardization of AAS

During the analysis on Atomic Absorption Spectroscope (Shimadzu-AA-6800), Multi elemental standard were procured from Merck (ICP multi-elemental standard VIII) and the instrument was standardized with respect to these standards.

3.5 Statistical Analysis

Digitization of the map was done using GEOMATICA and contours were drawn using SURFER Version 8.0.

The observed results were statistically analyzed using computer aided packages viz. EXCEL (Microsoft Office version 2003) SPSS version 10.5, and SIGMAPLOT version 2001.

Chapter 4

Results &
Dicussions

4.1 Post Tsunami Nutrient Chemistry in Pichavaram Waters

After tsunami, there were significant physiochemical changes in water column of the Pichavaram mangroves of southeast coast India (Table 4.1, 4.2, 4.3). Spatial variations in the nutrient concentration are important factors which might have influenced the biogeochemical behaviour of the nutrients in the Pichavaram mangrove waters. Hence our study was oriented in this direction. The mangrove water is alkaline in nature without any systematic spatial variation irrespective of seasons (Mook and Koene, 1975). The mean pH value of the Pichavaram mangrove water before tsunami was 7.81 (7.40-8.30, Ramanathan et al , 1999) and after tsunami its value is 7.70 (7.50-8.10). The higher pH values observed are due to the mixing of seawater with estuarine waters and by the mangrove photosynthetic activity, which utilized CO_2, thereby, shifting the equilibrium towards highly alkaline (Ruttner, 1953). There is a slight change in pH value after Tsunami.

The mean Electrical conductivity (EC) value of the Pichavaram mangrove water before tsunami was 37312 μS/cm (17500 - 43600 μS/cm; Ramanathan et al , 1999) and after tsunami its value increased to 42,106 (39,131-45,446). (Table 4.1, 4.3). Also the mean value of TDS before tsunami was 27,558 mg/L (9453 -40693 mg L^{-1}) (Ramanathan et al., 1999) and after tsunami was 28,892 mg/L (28,090-31,502). EC is minimal during the monsoon and maximal during non-monsoon. Thus, the influence of atmospheric precipitation on EC and total dissolved solids (TDS) is more pronounced in the mangrove during the monsoon period. The increase in the ionic strength of the mangrove water during the non-monsoon periods may be due to less river water input via estuaries due to the construction of dams, aided by evaporation due to an elevated temperature and friction due to high-speed wind activity in the region (Ramanathan et al., 1999).

The increased in EC and TDS value was due to highly saline sea water inundation via channels and its retreat after tsunami, which in turn, added the solute load from adjoin area, i.e. agricultural land human settlement as well as aqua culture pond beside marine water.

Table 4.1 Physico- Chemical parameters of Post tsunami water

Sample ID	**pH**	**EC (µS/cm)**	**TDS (mg/L)**	**ORP (mV)**	**DO (mg/L)**	**SAL (‰)**	**SO_4 (mg/L)**	**PO_4 (mg/L)**	**NO_3 (mg/L)**	**Cl (mg/L)**	**HCO_3 (mg/L)**	**NH_4 (mg/L)**
1	7.8	44427	31193	174	8.2	30.3	4300	7.10	16.41	15254	176.92	4.35
1A	8.1	43775	31188	175	7.7	29.1	4035	7.34	34.89	14912	171.15	6.09
2	7.6	40626	28773	179	7.9	26.6	3360	7.21	10.59	13981	109.73	3.54
4	7.5	41348	30563	172	8.1	28.3	3526	8.29	4.18	14666	121.00	10.30
6	7.6	39925	28563	178	8.3	26.0	2926	7.16	35.22	13050	100.75	6.14
7	7.6	42395	31503	178	9.1	27.8	2907	8.38	4.24	14974	163.33	10.43
7A	7.8	40326	28090	178	8.1	28.5	2779	8.00	88.90	14500	162.08	12.79
7B	7.7	41898	30200	172	8	28.0	3707	7.12	16.26	14115	175.31	4.31
8	7.5	39131	28633	175	8.6	26.0	3400	8.21	90.01	13844	164.10	12.95
9	7.6	42584	29560	174	8.9	28.0	3988	8.12	40.77	14422	128.21	7.11
10	7.7	43390	29385	179	8.7	29.4	4045	9.81	34.92	14922	109.81	6.09
11	7.9	45446	31063	176	8.4	30.5	4263	7.11	38.38	15403	120.71	6.69
Min	7.5	39131	28090	172	7.7	26.0	2779	7.10	4.18	13050	100.7	3.5
Max	8.1	45446.2	31502.5	179.0	9.1	30.5	4300.0	9.8	90.0	15403.2	176.9	12.9
Mean	7.7	42106.0	29892.5	175.8	8.3	28.2	3603.2	7.8	34.6	14503.5	141.9	7.6
SD	0.2	1928	1210	3	0.4	1.5	538	0.82	28.86	670	29.2	3.3

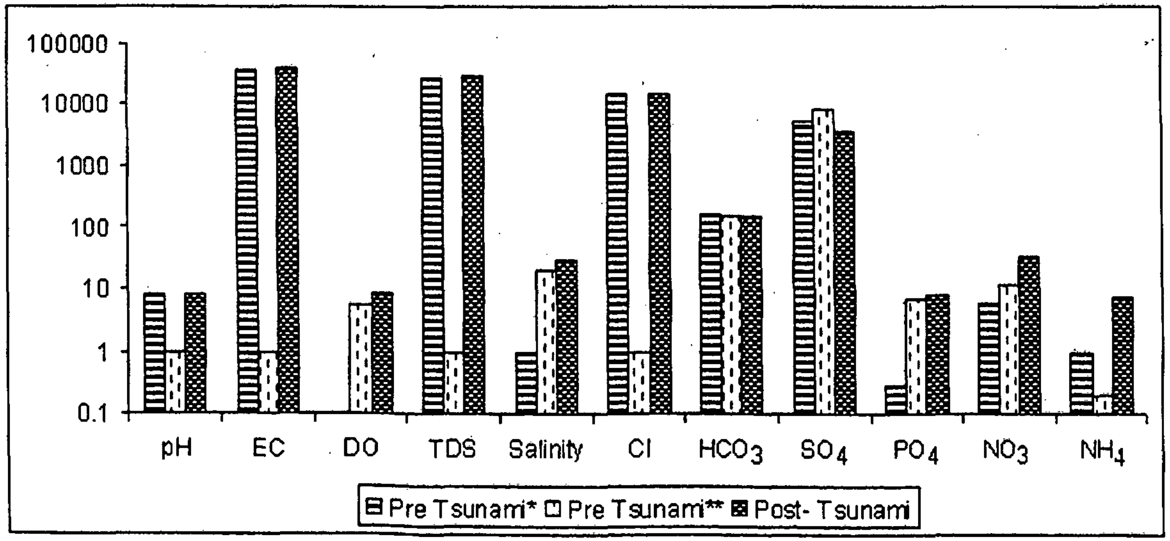
Table 4.2 Physico- Chemical Selected metal s of Post tsunami water

	Na (mg/L)	K (mg/L)	Ca (mg/L)	Mg (mg/L)	Fe (mg/L)	Mn (mg/L)	Ni (mg/L)	Zn (mg/L)	Cr (mg/L)	Cd (mg/L)	Pb (mg/L)
1	7544	208.73	302.72	1537	50.46	0.135	0.064	0.617	0.146	0.025	0.135
1A	7904	260.05	288.40	1558	33.13	0.025	0.026	0.410	0.128	0.010	0.138
2	6760	198.73	266.25	1457	68.33	0.450	0.146	1.325	0.805	0.012	0.145
4	6259	175.86	272.25	1338	33.79	0.035	0.053	0.520	0.646	0.003	0.184
6	5631	262.45	204.26	1382	33.44	0.025	0.026	0.414	0.130	0.010	0.139
7	6338	279.31	251.36	1361	34.21	0.035	0.054	0.526	0.654	0.003	0.187
7A	6319	230.39	233.54	1377	89.65	0.284	0.034	0.298	0.184	0.002	0.072
7B	7475	285.91	277.60	1460	50.00	0.134	0.063	0.611	0.144	0.025	0.134
8	6398	294.02	236.46	1569	90.77	0.288	0.034	0.302	0.186	0.002	0.073
9	6518	281.83	256.46	1606	38.71	0.029	0.030	0.479	0.150	0.011	0.161
10	6513	260.23	273.53	1606	33.15	0.025	0.026	0.410	0.128	0.010	0.138
11	7160	207.06	290.64	1534	36.45	0.027	0.028	0.451	0.141	0.011	0.152
Min	5631	176	204	1338	33.13	0.025	0.026	0.298	0.128	0.002	0.072
Max	7904	294	303	1606	90.77	0.450	0.146	1.325	0.805	0.025	0.187
Mean	6735	245	263	1482	49.34	0.124	0.049	0.530	0.287	0.010	0.138
SD	656	40	28	99	21.81	0.142	0.034	0.270	0.254	0.008	0.036

Table 4.3. Comparison between the Physico-Chemical Parameter of Pichavaram waters Pre-Tsunami and Post-Tsunami

	pH	EC	DO	TDS	Salinity	Cl	HCO_3	SO_4	PO_4	NO_3	NH_4	
Pre Tsunami*	7.8	37312.0		27558.0	-	14603.0	161.0	5171.0	0.3	5.9	-	*Ramanathan et al 1999
Pre Tsunami**	-	-	5.5	-	19.4	-	331.5	8600.32	6.9	11.7	0.2	**Prasad , 2005
Post- Tsunami	7.7	42106.0	8.3	29892.5	28.2	14503.5	149.4	3603.2	7.8	34.6	7.6	Present Study

Figure 4.1 .Comparison between the Physico-Chemical Parameter of Pichavaram waters Pre-Tsunami and Post-Tsunami



Salinity is an important factor, which is having direct and indirect control over the nutrient availability and their transformations in the saline aquatic environments (Dittmar and Lara, 2001; Ragueneau et al., 2002). Before tsunami (pre-tsunami, January 2004) salinity was 19.44 ‰ (Prasad 2006) and it was increased to 28.20 ‰ (26-30.50 ‰) after tsunami (Table 4.1, 4.3). This indicates that most of the intruded sea water was stored in the mangrove forest and was then successively released, since the residence time of water in the semi-enclosed mangrove lagoon was higher (Prasad et al., 2005).In monsoon, the salinity decreased drastically because of significant fresh water in flow from the Vellar and the Coleroon rivers. In non-monsoon periods, a strong salinity gradient was observed suggesting the presence of water masses of multiple origins (Prasad, 2005). Low salinity water was more evident during high tides in the monsoon and post-monsoon seasons than during low tides during the rest of the year. Correspondingly, oceanic water intrusion was stronger in the summer season. Uncles and Stephens (1996) showed that salinity intrusion was a strong function of the tidal state and a weaker function of fresh water inflow where most of nutrients showed conservative mixing.

Tsunami had created displacement of huge shallow/bottom by the surface waters, this rapid movement of water facilitated atmospheric oxygen to dissolve in the water column, thus DO was increased from 5.52 mg/L (4.21 -7.89 mg/L) to 8.3 (7.7-9.1 mg/L)

The dynamics of the DIC (HCO_3^-) in the mangrove water was directly controlled by the weathering phenomenon in and around the Pichavaram mangroves. The carbon was mainly derived from the carbonate weathering from the adjacent streams/distributries (Ramanathan et al., 1993). The spatial and temporal variation in the DIC dynamics was also a function of the biological activity. The biological activity had some direct control over the DIC dynamics in this mangrove water column. Before tsunami (January 1995 and January 2004) mean concentration of DIC was 161 mg/L (Ramanathan et al., 1999) and 331.48 mg/L (Prasad, 2005) respectively and it was decreased to 141.90 mg/L after tsunami (Table 4.1, 4.3). Higher amount of DIC in monsoon in the mangrove water may be due to lesser assimilation of carbon by the biological systems (Black and Shimield, 2003) and leaching from the deposited sediments. Sanudo-Wilhelmy et al., (2001) reported that carbon availability in the water column was directly related to the phosphorus dynamics. Since, this mangrove is semi-enclosed type and has high water residence time, thus retained water would stay for long time and allows maximum amount of carbon would be utilized by the biological systems. The oceanic water intrusion due to Tsunami might have significant influence over the fresh water as result the there have been a decrease in the bicarbonate concentration in the mangrove waters (Ramanathan et al., 1993)

Dissolved inorganic nitrogen (NO_3^- & NH_4^+) is important component in the biological activities The laboratory elutriate test results of Lee et al., 1978 showed that when anoxic condition were created during elutriation, many of the potential nutrient were released into water Mean NO_3^- concentration before tsunami is 5.9 mg/L (0.35-40.70 mg/L, Ramanathan et al., 1999) and 11.73 mg/L (5.24-13.24 mg/L; Prasad 2006) where as after tsunami its concentration was observed as 34.56 mg/L (4.18 -90.10 mg/L). The observed change in the DIN concentration after the tsunami is consistent and an increase in concentration of NO_3^- in mangrove water may be from leaching from agricultural field while inundated seawater. Further increased nitrification activity has resulted in oxidized nitrogen. It is evident that, the mangrove ecosystems are continuously impacted by the human pressures mainly from the effluents from the aquaculture fields and agricultural runoff (Trott and Alongi 2001). The Pichavaram mangrove faces degrading activity mainly from human disturbances (Alongi et al., 2005; Subramanian, 2004). A quite significant number of aquaculture ponds were there in this mangrove area and at the same time their demographic distribution was also significant. The retreating water currents might have carried huge loads of effluents and wastes from the adjacent aquaculture ponds, agricultural fields and human settlements and contribute to increasing NO_3^-.

Before Tsunami, Ammonium concentration accounted for a small fraction of total inorganic nitrogen but after tsunami the concentration of was increased in the order of magnitude 5µ Mole to 500µM indicating the intense nitrification of the system(Ramesh et al., 2006). Nitrogen fixation was the most important biochemical mechanism which has direct influence over the DIN dynamics in the mangrove water.

nitrogen into nitrate and nitrite. Since, mean residence time of water in this mangrove system was more (Prasad, 2005), nitrogen availability would be more and enhances the biological productivity. In combination with phosphate, this might have undergone some change to increase the eutrophication in the mangrove waters.

Ammonia contributes significantly to the biogeochemical Nitrogen pool in anoxic environment. Mean NH_4 concentration (0.22 mg/L) varied from 0.14 to 0.27 mg/L before tsunami (Prasad, 2006) where as after tsunami its concentration was 7.56 mg/L (3.54 -12.95 mg L^{-1}) (Table 4.1, 4.3). Ammonia levels in the mangrove water column influenced by the tidal wetting, plant uptake and seasonal changes in microbial decomposition, temperature and rainfall (Boto, 1982, 1984; Boto et al., 1985). Vertical distribution of ammonia in the mangrove mud is highly dependent on the redox state at a particular zone and also ammonia absorbed by the sediment particles thus, it stored considerable amount in the interstitial water. Any disturbances in the sediment column by various natural or human pressures, this stored ammonia would release into the surface waters and elevate its concentration by several folds. The impact of tsunami on ammonia distribution in the mangrove is highly conspicuous. The high energy water current while passing across the mangrove system has disturbed the sediment – water column, thus stored ammonia in the interstitial water might have dissolved into the surface water. In addition to this, redox state of the sediment column might have changed to oxic state; this would encourage desorbing absorbed ammonia by the sediment particles (Hendricks and White, 2000). Thus, the elevated ammonia in the water column may disturb the over all nitrogen distribution and dynamics across the mangrove system and this will be completely understood after careful integrated assessment of different pathways only through stable isotope study.

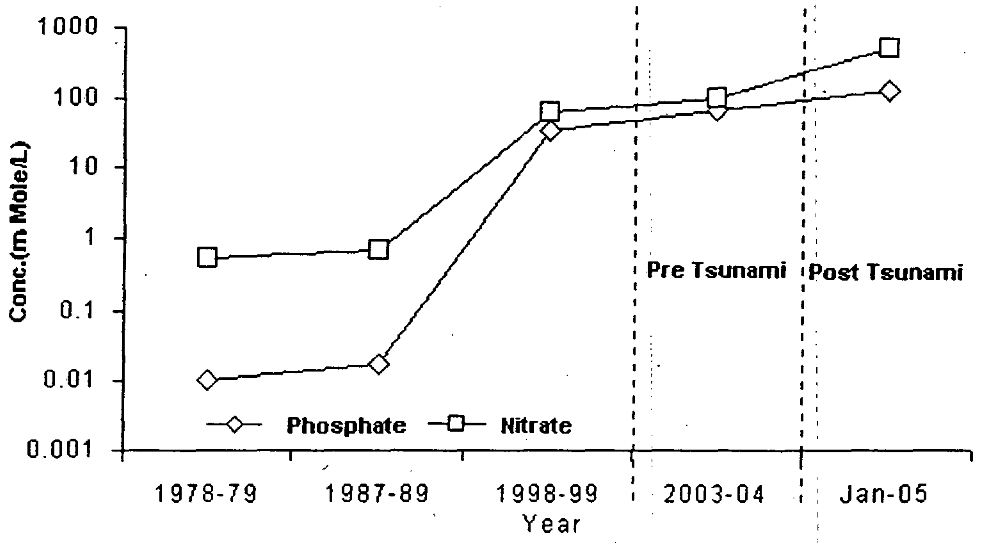
The diversity of the macrophyte population depends up on the nutrient load, more prominently N than P, in the ecosystem (Sundareshwar et al., 2003). In the Pichavaram mangrove, the macrophyte population diversity ranges from 1.6 x 10^3 to 9.2 x 10^4 (Kathiresan, 2000). Thus, biological rather than physical processes may be more important in regulating the nutrient distribution in the mangrove environment. P concentrations decrease with increasing salinity (Nixon et al., 1984; Robertson et

P concentrations decrease with increasing salinity (Nixon et al., 1984; Robertson et al., 1992) in dry periods in other mangrove waters (Sarala Devi et al., 1983; Balakrishna Nair et al., 1984), but in the wet season, the availability of P depends upon the nature of the sediment load (Alongi et al., 1992), and such may be the case in this Indian ecosystem. In contrast to DIN, DIP is usually buffered in estuarine/mangrove systems, being taken up when concentrations are high and released when they are low (Patrick and Khalid, 1974). There is also a rapid reduction of phosphorus during flocculation of metals, organic carbon and humic substances, as salinity increases to > 20 parts per thousand (Sholkovitz, 1976). Phosphorus may also readily adsorb onto the surface of sediments and lost from the water column as sediments deposit (Sundareshwar et al., 2003). Other major mechanisms for the removal of phosphorus from the water column are plant uptake, microbial incorporation and soil fixation (Patrick, 1992), and undoubtedly such processes must occur in this system. The fixation of phosphorus is more extensive and less reversible under alternating flooding-draining than under either continuously flooded or continuously moist soil conditions.

The mean concentration of PO_4 – P (DIP) concentration varied from 2.05 to 12.90 mg/L (Prasad 2005). Before tsunami mean PO_4^{-3} concentration in Pichavaram mangrove water was 0.24 mg/L (Ramanathan et al., 1999) and 6.01 mg L^- (Prasad, 2005), and increased to 7.82 mg/L (7.10 - 9.81) after tsunami As there have been extensive use of fertilizers {DAP (Di-Ammonium-Phosphate) and NPK} in the adjoining agricultural lands (Tandon, 1987; Ramanthan, 1999) the retreating water of Tsunami has brought the agricultural waste load to the mangrove forest. The higher concentration of the phosphate is as well derived from the Cretaceous formation rich phosphate nodules of Trichirapalli (Vaithiyanathan et al., 1989). Since, the highly reducing environment in the deeper layers of the sediment, much amount of P will be stored as PO_4^{-3} in the intestinal water. Alongi et al., (2005) reported a considerable amount of PO_4^{-3} in the pore waters of the Pichavaram mangroves (Table 4.1, 4.3). The main reason for little increase of PO_4^{-3} in the water may be direct input from the stored pore water and also from the terrestrial input from the aquaculture ponds and

Na is the dominant cation followed by Ca and K. The mean concentration of Na, and Ca in post tsunami mangrove water were 6735 mg/L (5631-7904 mg/L); and 263 mg/L (204-303 mg/L) respectively which was more than reported value in the monsoon season of January-1995, (Ramanathan et al., 1999). The K was lower in concentration than Na because sodium is more mobile than potassium and dominates the natural solutions. (Milliot 1970, Ramanathan et al., 1999) or K came from the sea water, which had less concentration K than Na and Ca. The mean concentration of the metals was as follow:- Fe - 49.34 mg/L (33.13 - 90.77 mg/L); Mn – 0.124 mg/L (0.025-0.45 mg/L); Ni - 0.049 mg/L (0.026-0.146 mg/L); Zn- 0.530 mg/L (0.298-1.325 mg/L); Cr - 0.287 mg/L(0.128-0.805 mg/L); Cd - 0.01mg/L (0.002-0.025 mg/L) and Pb - 0.130 mg/L (0.072-0.187 mg/L) respectively (Table 4.2, 4.3).

Figure: 4.2. Decadal changes in the major nutrients in the Pichavaram mangrove environment



(Redrawn from Prasad, 2005 and Present Study).

There has been sheer increase in phosphate and nitrate concentration in the Pichavaram mangrove environment. As mention earlier (in section 4.2), during the past decades their have been a rapid increase in the number of aquaculture ponds as well as the cultivation pattern has changed drastically. As a results the waste are past decades their have been a rapid increase in the number of aquaculture ponds as well as the cultivation pattern has changed drastically. As a results the waste are being transferred to the estuarine complexes through Vellar Estuary, Uppnar Estuary and Khan Sahib Canal (Yeon CHO et al., 2004), thus increasing Nitrogen and phosphorus load to the mangrove environment. Further increase after tsunami is attributed to the retreating water which carried the waste from the agricultural fields and aquaculture ponds to this ecosystem.

The inter nutrient correlations were given in Table 4.4. The good correlation between salinity – Na; salinity, Cl^- and SO_4^{2-}; Na –SO_4^{2-}; and Ca – Cl^- showed that inundated seawater had intruded and retreating water loaded these ions into the Pichavaram mangrove area. As revealed by Ca contribution, which is third after Na and Mg in sea water. SO_4^{2-}contributed next highest anion in the sea water after Cl^-, whereas mean concentration K and SO_4^{2-} was less than the reported value.

Salinity showed significant correlation (at significance level 5%) with Na, Ca, Cl SO_4^{2-}, EC and TDS, which indicated that oceanic water, had strong influence on the mangrove water. Significant correlation between Na and Cl, Ca with Cl indicated that these ions were oceanic in origin. However significant correlation between Na and bicarbonate indicated that bicarbonate weathering was also an important geochemical process contributing to the water. The decrease in the bicarbonate concentration may be attributed to dilution by sea water (Ramanathan et al., 1993).

Table 4.4 Correlation Matrix of Physico-Chemical Parameters of Pichavaram water – Post Tsunami

(n = 12)

	pH	**EC**	**TDS**	**ORP**	**DO**	**SAL**	**SO_4**	**PO_4**	**NO_3**	**Cl**	**HCO_3**	**NH_4**	**Na**	**K**	**Ca**	**Mg**
pH	1.00															
EC	**0.64**	1.00														
TDS	0.40	**0.78**	1.00													
ORP	0.02	-0.17	-0.41	1.00												
DO	-0.45	0.04	0.05	0.22	1.00											
SAL	**0.67**	**0.89**	**0.62**	-0.19	-0.07	1.00										
SO_4	0.45	**0.79**	**0.51**	-0.42	-0.09	**0.69**	1.00									
PO_4	-0.33	-0.04	-0.16	0.27	**0.57**	0.02	-0.07	1.00								
NO_3	0.08	-0.42	-0.62	0.17	0.06	-0.17	-0.21	0.15	1.00							
Cl	**0.52**	**0.84**	**0.73**	-0.13	0.12	**0.90**	**0.58**	0.18	-0.22	1.00						
HCO_3	0.34	0.15	0.35	-0.41	-0.13	0.21	0.05	-0.21	0.18	0.29	1.00					
NH_4	-0.30	-0.48	-0.24	0.03	0.34	-0.23	-0.53	0.42	**0.60**	-0.03	0.22	1.00				
Na	**0.73**	**0.67**	**0.59**	-0.41	-0.47	**0.60**	**0.70**	-0.41	-0.21	**0.55**	**0.56**	-0.50	1.00			
K	-0.09	-0.19	-0.15	0.03	0.46	-0.37	-0.15	0.22	0.33	-0.33	0.32	0.15	-0.07	1.00		
Ca	**0.51**	**0.82**	**0.72**	-0.41	-0.27	**0.78**	**0.82**	-0.13	-0.45	**0.78**	0.28	-0.48	**0.84**	-0.38	1.00	
Mg	0.31	0.44	0.05	-0.08	0.16	0.31	**0.76**	0.16	0.26	0.26	0.06	-0.31	0.46	0.32	0.41	1.00

4.2 Sediment Biogeochemistry

4.2.1 Physical Characterization

4.2.1 .1 Granulometric Studies

Grain size distribution has been used for the determination of sedimentary environment with the help of log-probability studies. The entire grain size distribution is believed to be considered of several normal subpopulations representing the sediments transported by the process of rolling, suspension and saltation (Inman, 1949). Textural attributes of sediments and sedimentary rocks viz. Mean (Mz), Standard deviation (σ_I), Skewness (Sk_I) and Kurtosis (K_G) are widely used to reconstruct the depositional environments of sediments and sedimentary rocks (Amaral, 1977).

The size analysis of the sediments from various locations showed one surface creep, either one or two saltation and one suspension. About 95% of the surface samples exhibit the fine fraction at less than 95% and coarse truncation at about 5% and others exhibit the fine truncation more than 90% and coarse truncation below 10%.

4.2.1.2 Mean (Mz)

It is the average size of the sediments and is influenced by the source of supply, transporting medium and the energy conditions of the depositing environment. Mean size indicates the central tendency or the average size of the sediment and in terms of energy; it indicates the average kinetic energy / velocity of depositing agent (Sahu, 1964).

Surface samples from Chinnavaikkal (1-2), inside of mangrove forest (1-3), Coleroon Estuary (1-3) MGR Tittu and Near Vellar estuary showed fine sediment characteristics. The post tsunami mean size ranged between 2.39Φ (Coleroon estuary) to 3.46Φ (near Vellar estuary). The average mean size was 2.77 (Fig. 4.3) The post tsunami sediments indicated the presence of very fine to fine sand and the average size indicated the dominance of fine sand. The pre tsunami sediments mean size ranged between 1.9Φ to 3.06Φ. The average mean was size 2.38Φ. The pre tsunami samples indicated that sand was medium to very fine sand and the average mean size was that of fine sand. The fine grain nature indicated that the moderately low energy condition in the basin of deposition. Sands deposited by tsunami almost invariably contained fine particles from suspended

Table 4.5 Result of Statistical Analysis of Pre Tsunami Sediments (Ramanathan et al 1999)*

Location	Mz	Std	Ski	Ka	Remarks				Energy Process
Near Vellar Estuary	2.53	0.34	0.26	1.28	Fine sand	Very well sorted	Fine Skewed	Leptokurtic	Beach process
MGR tittu	2.23	0.88	0.1	0.83	Fine sand	Moderately sorted	Fine Skewed	Platykurtic	Inner shelf
Chinnavaikal-1	2.28	0.85	0.52	0.62	Fine sand	Moderately sorted	Very Fine Skewed	Very Platykutic	Inner shelf
Chinnavaikal-2	2.93	0.76	0.23	0.52	Fine sand	Moderately sorted	Fine Skewed	Very Platykutic	Inner shelf
Inside the Mangrove Forest-1	2.7	1.04	0.2	0.58	Fine sand	Poorly Sorted	Fine Skewed	Very Platykutic	Inner shelf
Inside the Mangrove Forest-2	3.06	0.9	0.19	0.85	Fine sand	moderately sorted	Fine Skewed	Mesokutic	Inner shelf
Inside the Mangrove Forest-3	2.25	0.96	0.12	0.55	Fine sand	moderately sorted	Fine Skewed	Very Platykutic	Inner shelf
coleron estuary-1	1.96	0.4	0.56	0.89	Medium Sand	well sorted	Very Fine Skewed	Platykurtic	Beach process
coleron estuary-2	2	0.44	0.51	0.97	Medium Sand	well sorted	Very Fine Skewed	Mesokutic	Beach process
coleron estuary-3	1.9	0.4	0.52	0.98	Medium Sand	well sorted	Very Fine Skewed	Mesokutic	Beach process

* *Folk And Ward, 1957*

Table 4.6 Result of Statistical Analysis of Tsunamigenic Sediments*

Location	Mz	Std.D	Ski	Ka	Remarks				Energy Process
Near velar Estuary (1)	3.46	0.84	-0.02	1.23	Very Fine sand	Moderately Sorted	Nearly Symmetrical	Leptokurtic	Inner Shelf
MGR tittu 1 (1A)	2.42	0.57	-0.52	0.6	Fine sand	Moderately Well Sorted	Coarse Skewed	Very Platykurtic	Beach Process
Chinavaikal-1 (2)	2.45	0.57	-0.56	0.58	Fine sand	Moderately Well Sorted	Coarse Skewed	Very Platykurtic	Beach Process
Chinnavaikkal-2 (3)	2.98	0.8	-0.07	1.16	Fine sand	Moderately Sorted	Nearly Symmetrical	Leptokurtic	Inner Shelf
Inside of mangrove forest-1 (6)	2.86	1.11	1.4	2.11	Fine sand	Poorly Sorted	Very Fine Skewed	Very leptokurtic	Inner Shelf
Inside of mangrove forest-2 (7)	3.07	1.42	2.36	3.37	Very Fine sand	Poorly Sorted	Very Fine Skewed	Extremely leptokurtic	Quite Water
Inside of mangrove forest-3 (8)	2.47	1.67	6.8	4.74	Fine sand	Poorly Sorted	Very Fine Skewed	Extremely leptokurtic	Inner Shelf
Coleron estuary-1 (9)	2.48	0.71	-0.1	0.72	Fine sand	Moderately Sorted	Coarse Skewed	Platykurtic	Inner Shelf
Coleron estuary-2 (10)	3.15	1.09	0.52	2.06	Very Fine sand	Poorly Sorted	Very Fine Skewed	Very leptokurtic	Quite Water
Coleron estuary-3 (11)	2.39	0.97	-0.6	1:65	Fine sand	Moderately Sorted	Coarse Skewed	Very leptokurtic	Inner Shelf

* *Folk And Ward, 1957*

*Table No: 4.7 Showing Linear Discrimination** values in Pre Tsunami Sediments(Ramanathan et al 1999)*

Location	Y1	Y2	Y3	Y4	Remarks			
Near Vellar Estuary	-5.16	75.59	-1.5	10.3	Aeolain	Shallow Marine	Shallow Marine	Fluvial
MGR tittu	-2.72	102.96	-6.6	6.36	Beach	Shallow Marine	Fluvial Deltaic	Turbidity Current
Chinnavaikal-1	-4.61	104.05	-8.19	8.14	Aeolain	Shallow Marine	Fluvial Deltaic	Turbidity Current
Chinnavaikal-2	-7.18	97.6	-5.32	6.18	Aeolain	Shallow Marine	Fluvial Deltaic	Turbidity Current
Inside the Mangrove Forest-1	-4.24	127.69	-9.66	5.93	Aeolain	Shallow Marine	Fluvial Deltaic	Turbidity Current
Inside the Mangrove Forest-2	-5.67	120.29	-7.11	7.66	Aeolain	Shallow Marine	Fluvial Deltaic	Turbidity Current
Inside the Mangrove Forest-3	-3.16	108.13	-7.99	4.97	Aeolain	Shallow Marine	Fluvial Deltaic	Turbidity Current
Coleron estuary-1	-4.79	67.8	-3.54	9.83	Aeolain	Shallow Marine	Fluvial Deltaic	Fluvial Deltaic
Coleron estuary-2	-4.46	71.21	-3.57	9.93	Aeolain	Shallow Marine	Fluvial Deltaic	Fluvial Deltaic
Coleron estuary-3	-4.22	67.8	-3.36	9.99	Aeolain	Shallow Marine	Fluvial Deltaic	Fluvial Deltaic

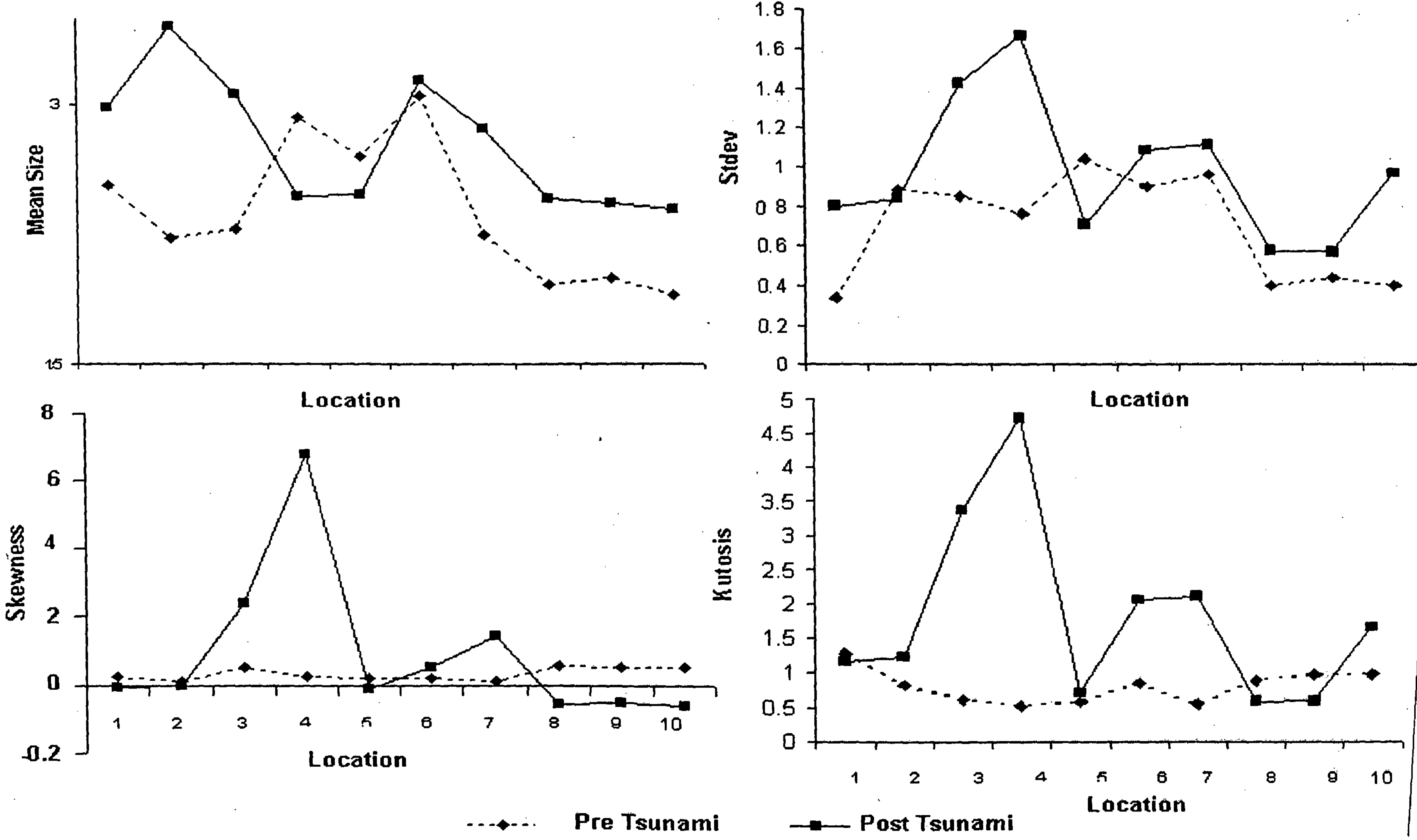
** *Sahu,1964*

*Table No: 4.8 Showing Linear Discrimination** values in Tsunamigenic Sediments (Present Study)*

Location	Y1	Y2	Y3	Y4	Remarks		
Near velar Estuary (1)	-5.87	122.77	-5.04	8.57	Aeolain	Shallow Marine	Shallow Marine
MGR tittu (1A)	-4.5	60.95	0.42	1.29	Aeolain	Beach	Shallow Marine
Chinavaikal-1 (2)	-4.55	60.71	0.57	0.99	Aeolain	Beach	Shallow Marine
Chinnavaikkal-2 (3)	-4.53	108.7	-4.32	7.55	Aeolain	Shallow Marine .	Shallow Marine
Inside of mangrove forest-1 (6)	-1.99	190.5	-16.78	22.16	Beach	Shallow Marine	Fluvial Deltaic
Inside of mangrove forest-2 (7)	2.15	286.3	-28.27	35.16	Beach	Shallow Marine	Fluvial Deltaic
Inside of mangrove forest-3 (8)	2.07	431.73	-56.64	71.5	Beach	Shallow Marine	Fluvial Deltaic
Coleron estuary-1 (9)	-4.56	82.93	-3.11	4.67	Aeolain	Shallow Marine	Shallow Marine
Coleron estuary-2 (10)	-1.54	174.08	-11.86	16.17	Beach	Shallow Marine	Fluvial Deltaic
Coleron estuary-3 (11)	1.33	118.71	-4.49	6.03	Beach	Shallow Marine	Shallow Marine

** *Sahu,1964*

Fig. 4.3: Variation of Pre and Post Tsunami Sediments Characterstics



load. Sands deposited on the parts of mangroves where the breaking waves continuously wash thin sheets of back and forth invariably lacked mixtures of fine-grained sediments. Fine-grained nature of sediments in the study region shows that they were deposited by inner shelf processes. Bigger tsunami waves scoured sediments when they hit the shallow shelf regime and deposited them in inland as suspended load during regression. The pre tsunami energy process included inner shelf and beach process.

4.2.1.3. Standard Deviation

It is expressed by inclusive graphic standard deviation (σ_I) of Folk and Ward (1957), as it covers both the tails of the distribution. Standard deviation is a poorly understood measure that depends on the size range of the available sediments, rate of depositing agent and the time available for sorting. The sorting variations observed attributed to the difference in water turbulence and variability in the velocity of depositing current. The moderately well sorted character of the sediments indicated the influence of stronger energy conditions of the depositing agents or prevalence of strong energy conditions in the basin. The post tsunami standard deviation values of the samples ranged between 0.57Φ (Chinnavaikkal and MGR Tittu) to 1.42Φ (inside of mangrove forest). The average standard deviation value is 0.97Φ (Fig. 4.3). About 20% of the sample indicates that they were moderately well sorted and 40% shows poorly sorted nature. The pre tsunami standard deviation ranged between 0.34Φ to 1.04Φ. The average standard deviation value was 0.7Φ. These values indicated that 50% of moderately sorted and 40% of well sorted. In the post tsunami sediments sorting characters showed drastic change in this mangrove areas.

4.2.1.4 Skewness

It is used to determine the symmetry of the central part of the distribution. It reflects the symmetry or asymmetry of the frequency distribution of the sediments. It is the measure of particle size sizes as it indicates that particles in excess of the normal distribution are present in coarser fraction or finer fraction, extremes of the distribution. If the skewness is negative, the sample is coarsely skewed, that is the mean is towards the coarser side of the median. When the skewness value is positive the sample is described as finely skewed. Coarsely skewed sample implies that the velocity of the depositing agent operated at a higher value than the average velocity for a greater length of time than normal and / or the velocity fluctuations towards the higher values occurred more often than normal (Sahu, 1964).

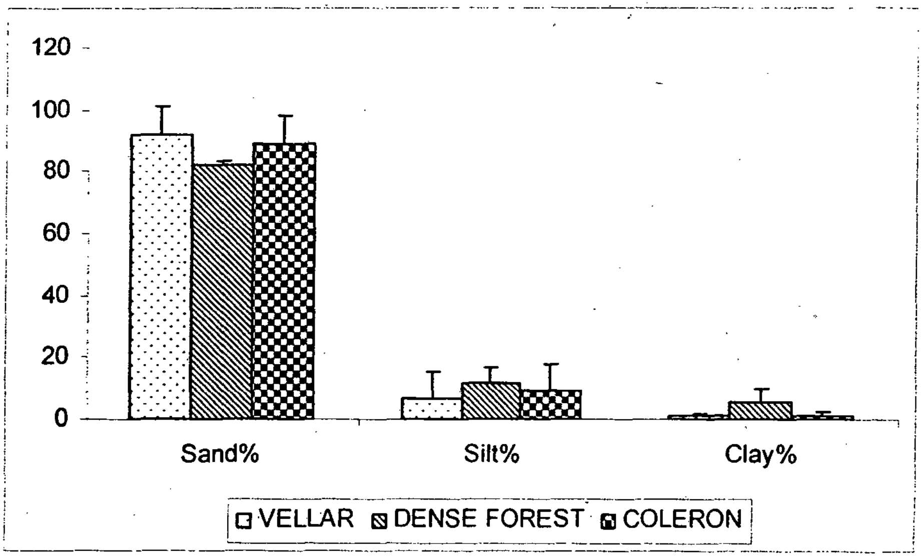
The post tsunami surface samples showed the skewness values ranging between –0.60Φ (Coleroon estuary-3) to 6.80Φ (inside of mangrove forest-3) with an average skewness value of 0.92Φ (Fig. 4.3). The values were indicative coarse skewed and very fine skewed. The pre tsunami surface samples showed the skewness values ranging between 0.1Φ to 0.56Φ with an average skewness value of 0.32Φ. The values were indicative of very fine skewed nature of the sediments. The pre tsunami sediments are positive deposition in this mangrove area. The post tsunami sediments showed deposits positive and negative as well ass negative skewed sediments.

4.2.1.5 Kurtosis

It is a measure of sorting of grain size. According to Folk (1966), it is also a function of internal sorting or distribution. The pre tsunami kurtosis values were 0.52 to 1.28 with an average of 0.81. After tsunami kurtosis values of the surface sediments vary between 0.58 (Chinnavaikal-1) to 4.74 (inside of mangrove forest-3) with an average of 1.82 (Fig. 4.3). About 50% of the samples were very platykurtic, 10% are platykurtic and 40% were leptokurtic in nature of distribution. . The indicated very platy kurtic to leptokurtic with a mesokutic.

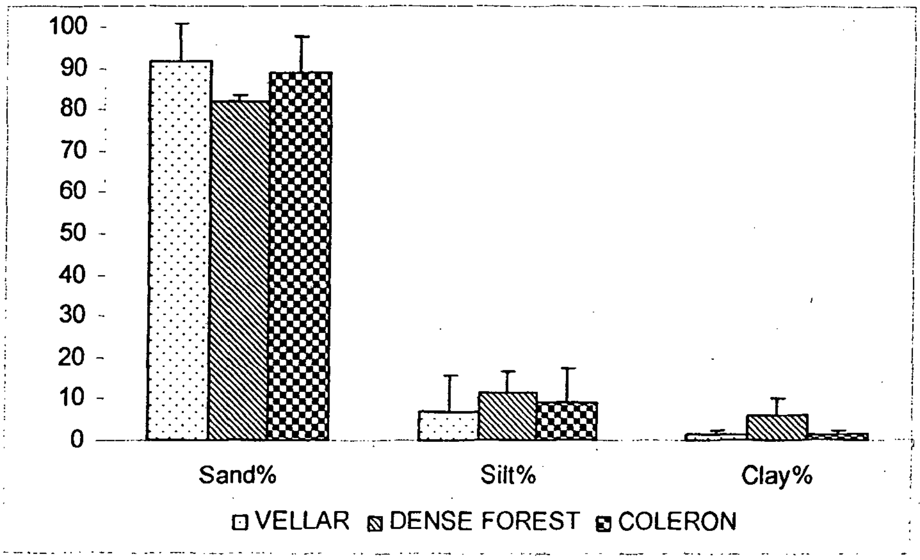
The leptokurtic nature of the sediments indicated the higher kurtosis values and the mixing of a predominant population with very minor amounts of coarser and finer materials (Mason and Folk, 1958; Prabhakara Rao et. al., 2001). The mesokurtic

Fig. 4.4 Variation of sediments nature in Pre-Tsunami Sediments



(Prasad, 2005)

Fig. 4.5 Variation of sediments nature in Post-Tsunami Sediments



character of the sediments indicated moderate winnowing action of the depositing agent. The mesokurtic nature of the sediments in the study area suggested that the sediments achieved good sorting in the high-energy environment. Platykurtic nature indicated poor winnowing without any sorting, i.e. all size fractions jumbled up. The leptokurtic behavior of the sediments also indicated the variations of the energy conditions of the environmental setup of depositions of the sediments. The leptokurtic character reflected the extreme skewness values, either positive or negative, indicating concentration of coarser and finer grained materials finally showing the impact of fluctuation of energy condition in the deposition of the sediments from most of the formations. The coarse grained character showed the influence of higher energy conditions and accumulation of finer materials show the influence of moderate to low energy conditions in the environmental setup showing the leptokurtic character of the sediments.

4.2.2 Depositional Environment

Depositional sedimentary environment had been variously defined. A depositional environment can be defined in terms of physical, biological, chemical or geomorphic variables. Thus, a depositional sedimentary environment is a geomorphic unit in which deposition takes place. This is characterized by a unique set of physical, biological and chemical processes operating at a specified rate and intensity, which imparts sufficient imprint on the sediment. The character of a sediment so produced is determined both by the intensity of the formative processes operating on it and by the duration through which such action is continued (Pettijohn, 1957). The study of physical factors (hydrodynamic condition), if combined with the study of biological and chemical factors provides a more complete picture of the sedimentary depositional environment (Reinck and Singh, 1980).

A broad depositional environment may be subdivided into smaller, essentially uniform sub environment or sedimentation units, where sediments with their own characteristic features are deposited. These units in ancient sediments are lithosomes (Wheeler and Mallory, 1956). As sedimentation proceeds, with time facial boundaries migrate laterally under the influence of transgression and regression, and different facies are arranged in an orderly sequence (Reinck and Singh, 1980). Curray (1964) gives a thorough discussion on transgression-regression processes and their effect on coastal sediments. The products of transgression and regression depends upon various factors, such as rate and supply of sediments, intensity of hydrodynamic processes, configuration of basin of sedimentation, local tectonics and rate and direction of relative sea level changes. All these factors can be grouped into two parameters- (a) rate of deposition, and (b) rate and direction of relative sea level change (Curray, 1964).

According to Sahu (1964), the variations in the energy and fluidity factors seem to have excellent correlation with the different processes and the environment of deposition. Sahu's linear discriminant functions of Y1 (Aeolian, beach), Y2 (Beach, Shallow marine), Y3 (Shallow Marine, Fluvial) and Y4 (Turbidity, Fluvial) were used to decipher the process and environment of deposition. With reference to the post tsunami sediments Y1 values, all the samples fall under Aeolian processes and except inside of mangrove forest (1-3) Coleroon estuary-2 and MGR Tittu (beach process), Y2 vales are fall in shallow marine except Chinnavaikkal-1 and MGR Tittu (beach). With reference to Y3 to Y4 values all the samples exhibit shallow marine deposition and turbidity current condition except Coleroon estuary-2 and inside of mangrove forest (1-3) deposits fluvial deltaic. According to the energy process diagram of mean Vs Standard Deviation shows that ten samples fall under inner shelf and two samples of exhibit beach process chinnavaikal-1 and MGR Tittu and quite water (Inside of Mangrove forest-2 and Coleroon estuary-2) (Table No. 4.5-4.8). The pre tsunami sediments Y1 and Y2 vales are Aeolain shallow marine process. Y3 vales are all samples are fluvial deltaic process except velar estuary shallow marine process. Y4 values all samples are turbidity current except Coleroon estuary and velar estuary samples. According to energy process inner shelf except Coleroon and Vellar estuaries (Table no 4.5-4.8). The post tsunami sediments are highly deposited in estuary areas according to energy process.

4.3 Biogeochemistry of Tsunamigenic Sediment

4.3.1 Surfacial Sediments

Mangrove forests are best developed on tropical shorelines where there is an extensive suitable intertidal zone, with an abundant supply of fine grained sediment, and are most luxuriant in areas of high rainfall or abundant fresh water supply through or river discharge. Thus, the mangrove sediments acts as both source and sink of nutrients of the overlying water column.

The distribution of Total Carbon (T.C), Total Nitrogen (T.N), Total Phosphorus (T.P) and Organic Carbon (O.C) in the tsunamigenic Pichavaram sediments is given in Table 4.9. The average concentration of total carbon in the tsunamigenic Pichavaram sediments was observed as 14.46±4.0 X 10^3 µg/g , organic carbon as 10.18 ± 3.48 X 10^3 µg/g, total nitrogen as 0.95±0.82 X 10^3 µg/g, total phosphorus as 0.77 ± 0.10 X 10^3 µg/g and average total sulfur was found to be 7.22±0.08 X 10^3 µg/g. The organic carbon was about 70% of the Total carbon. This high amount of the organic carbon was mainly because of the presence of fine-grained materials (Ramanathan, 1997) as well as due of the inherent biological productivity within the mangrove. Decomposition of organic foliage and other vegetative matter and their resuspension also contributed substantially to the organic matter content in the mangrove sediments (Singh et al., 2005).

The distribution of TC in the Pichavaram mangrove sediments was observed to be controlled by the grain size. It has been observed that the grain size fraction <10 µm having higher amount of TC than any other grain size, which account for 42.16% followed by 63-10 µm, 125-63 µm > 125 µm. This indicated that finer fractions have considerable surface area, which consequently leads to increased sorption of more carbon. And the combined effects of the physical condition of water flow, sediment load and geological settings are mainly responsible for such kind of behavior in the aquatic ecosystems (Probst et al., 1994). It was observed that the total carbon content decreased from 24.37 X 10^3 µg/g (Prasad, 2005) to 14.46 X 10^3 µg/g. However, interestingly organic carbon has increased drastically from 2.00 X 10^3 µg/g to 10.18 X 10^3 µg/g. It may be due to the fact that the retreating water carried the waste water from aquaculture, agriculture and other anthropogenic activity, which was ultimately trapped at the sediment owing to the characteristics nature of the mangrove ecosystem (Kathiresan, 2005). The concentration of total nitrogen varies with sediments type (higher in finer deposits (Boto and Wellington, 1984). Table 4.9 shows the mean concentration of total extractable nitrogen and phosphorus in some tropical mangrove sediments. The total nitrogen concentration generally ranges from 0.2 to 0.4 % of sediments dry weight (Alongi, 1992). The average concentration of nitrogen in sediments decreased significantly from 6.62 X 10^3 μg/g to 0.95 X 10^3 μg/g. As mentioned earlier, the scooping effect and the disturbance caused by Tsunami lead to nitrification of overlying water and as a result the nitrogen adsorbed to the sediment was released into the water.

Phosphorus is an important nutrient for the biological systems. In most of the aquatic systems, phosphorus is the limiting nutrient for the biological productivity. After Tsunami the concentration of phosphorus increased from 0.41 X 10^3 μg/g (Prasad, 2005) to 0.77 X 10^3 μg/g. The P concentration was also controlled by the grain size; the phosphorus concentration was dominated in < 10-μm grain size, compared to higher grain size. Fe levels in the surfacial sediments control the P dynamics in the sediment. In oxic conditions, Fe actively combines with P and made it unavailable (Hendricks and White, 2000). Towards the estuarine environment, P levels were low. Ramanathan et al., (1999) reported that Fe in the Vellar and Coleroon estuaries were higher than the Pichavaram mangrove sediments. Higher concentrations of Iron were observed in the present study too (average. 24,998 μg/g) Iron(III) in oxic environment was effective in quenching Phosphorus to form FeOOH-P, by which in marine sediments P is scavenged,

Since residence time of water in mangrove area is greater than the adjacent estuary regions (Prasad, 2005) which resulted into more interaction of P forms with different grain size particle in prevailing environmental conditions. Consequently higher concentration of P fraction was obtained.

Sulfur in the marine sediments has received considerable importance due to the pivotal role of sulfate reduction in the anaerobic respiration and the resultant production of authigenic sulfide minerals (Goldhaber and Kalpan, 1974). After tsunami the S concentration had increased considerably. The mean concentration of S

Table 4.9 C, N, P, S, OC and C/N distribution in the Pichavaram mangrove sediments. (values are in X 10^3 µg/g)

Samples	T C	I.C.	O.C.	S	P	N	C/N	N/P
1	10.85	2.75	8.11	7.35	0.65	0.76	14.38	1.17
1A	4.6	2.89	1.71	7.23	0.9	0.4	11.46	0.44
2	15.58	4.21	11.36	7.17	0.93	0.96	16.23	1.03
4	17.16	4.56	12.6	7.12	0.91	1	17.16	1.1
6	19.56	4.2	15.36	7.3	0.71	1.1	17.8	1.55
7	15.48	4.51	10.98	7.11	0.81	0.79	19.5	0.98
7A	16.07	4.23	11.84	7.21	0.7	0.9	17.95	1.29
7B	11.61	4.07	7.55	7.28	0.68	0.94	12.35	1.38
8	18.48	5.83	12.65	7.29	0.7	1.24	14.85	1.77
9	13.58	5.43	8.15	7.17	0.81	1.19	11.45	1.47
10	14.56	4.32	10.24	7.27	0.81	0.95	15.27	1.17
11	15.95	4.29	11.65	7.14	0.66	1.19	13.44	1.8
min	**4.6**	**2.75**	**1.71**	**7.11**	**0.65**	**0.4**	**11.45**	**0.44**
max	**19.56**	**5.83**	**15.36**	**7.35**	**0.93**	**1.24**	**19.59**	**1.8**
AVERAGE	**14.46**	**4.27**	**10.18**	**7.22**	**0.77**	**0.95**	**15.15**	**1.26**
S.D.	**4**	**0.86**	**3.48**	**0.08**	**0.1**	**0.23**	**2.66**	**0.37**

Table 4.10 Comparison of Total Phosphorus and total Nitrogen in world mangroves

Location	**Depth (cm)**	**TN (%)**	**TP(%)**	**Reference**
Pichavaram, India (Post tsunami)	0-50	0.02-0.2	0.062-0.099	Present study
Pichavaram, India (Pre tsunami)	0-60	0.02-0.25	0.02-0.058	Prasad et al, 2006
Sierra Leone, West Africa	0-10	-	0.08-0.16	Hesse, 1961, 1963
Florida Bay, USA	0-50	0.2-0.4	-	Rosenfeld. 1979
Hinchinbrook Island,Australia	0-100	0.1-0040	0.022-0.054	Boto and Wellington,1984
Sunderban, India	0-25	0.06-0.09	0.01-0.048	Sahoo et al., 1985
Queensland estuaries,Australia	0-2	0.02-0.40	0.011-0.067	Alongi, 1987
Goa, India	0-2	0.02-0.16		Japtap, 1987
Iriomote Island, Japan	0-5	0.05-0.09	0.022-0.038	Kuraishi et al.,1985
Phuket, Thailand	0-10	0.08- 0.10	-	Kristensen et al.,1988

Fig. 4.6 Variation of Total Carbon (T.C.) with grain size in tsunamigenic Pichavaram Sediments

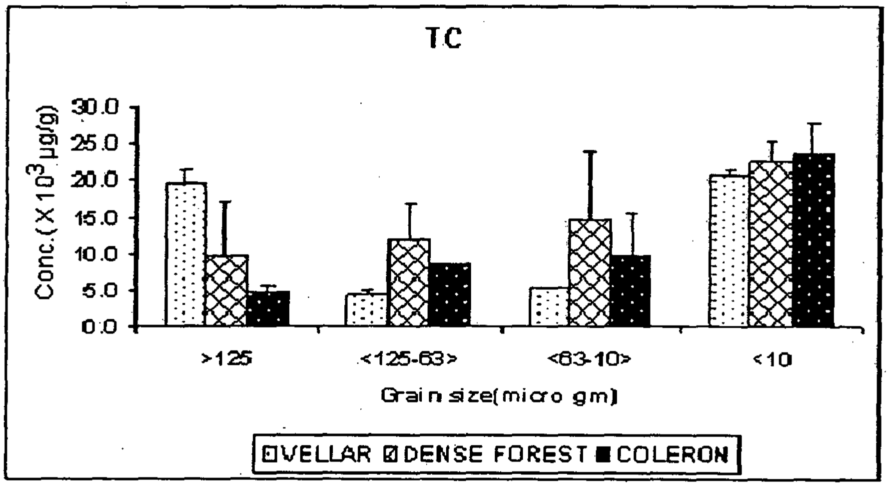


Fig. 4. 7 Variation of Total Nitrogen (T.N.) with grain size in tsunamigenic Pichavaram Sediments

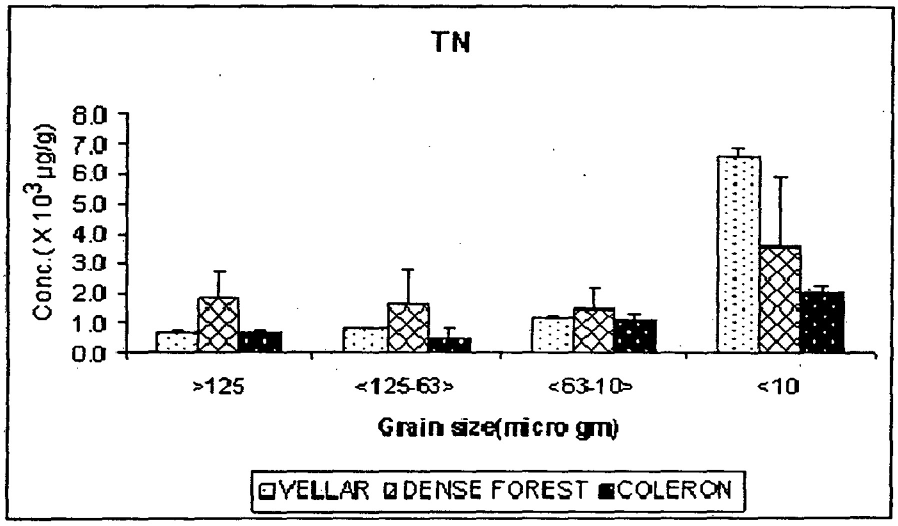


Fig. 4.8 Variation of C/N ratio with grain size in tsunamigenic Pichavaram Sediments

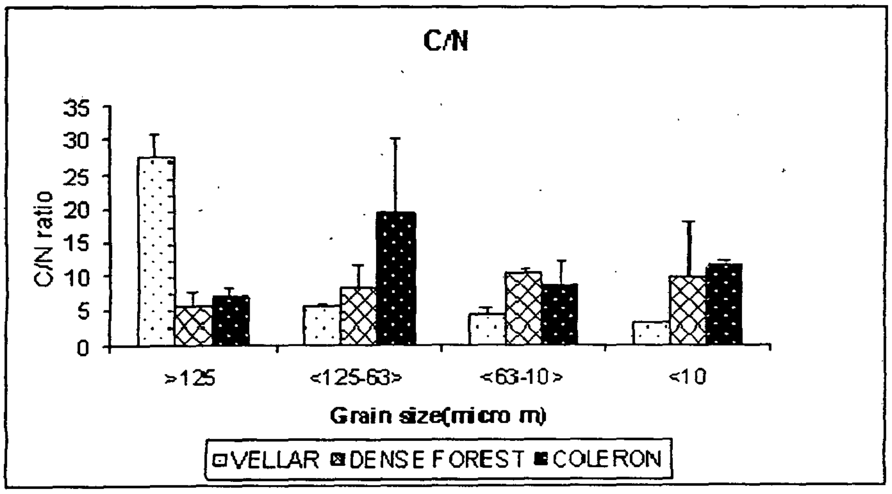


Fig. 4.9 Variation of Total Phosphorus (TP) with grain size in tsunamigenic Pichavaram Sediments

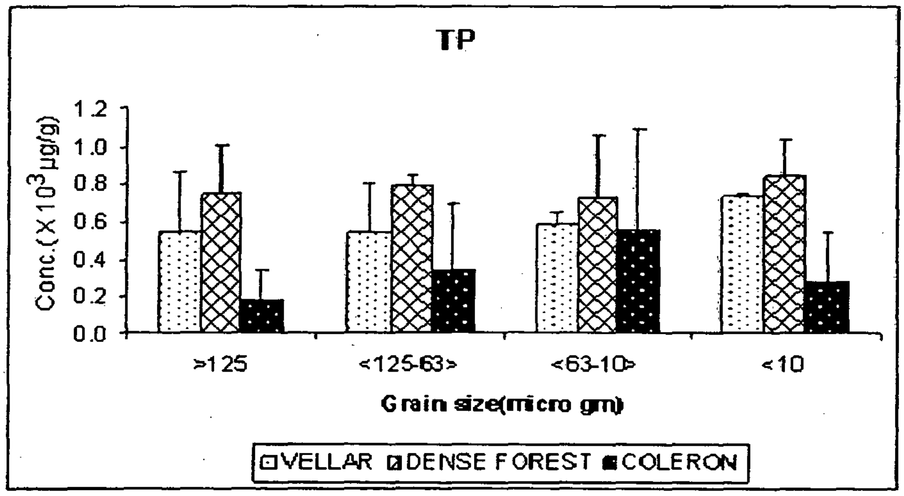


Fig. 4.10 Variation of Total Sulfur (TS) with grain size in tsunamigenic Pichavaram Sediments

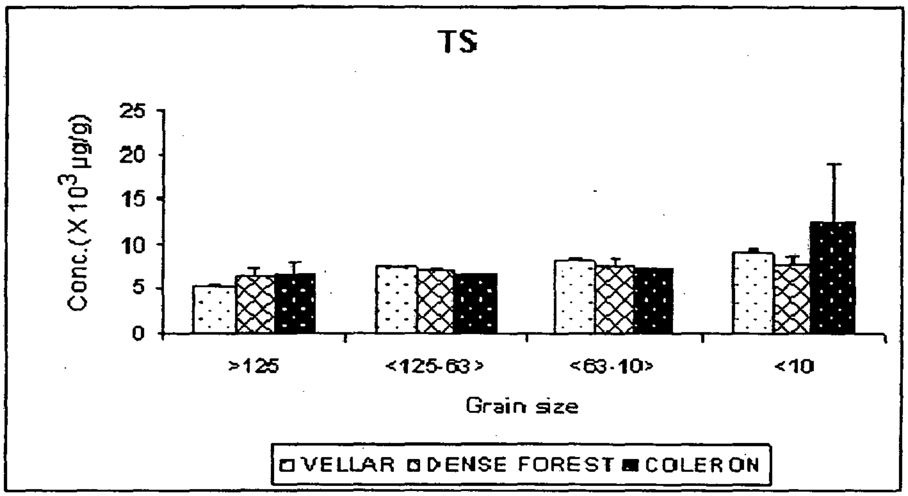
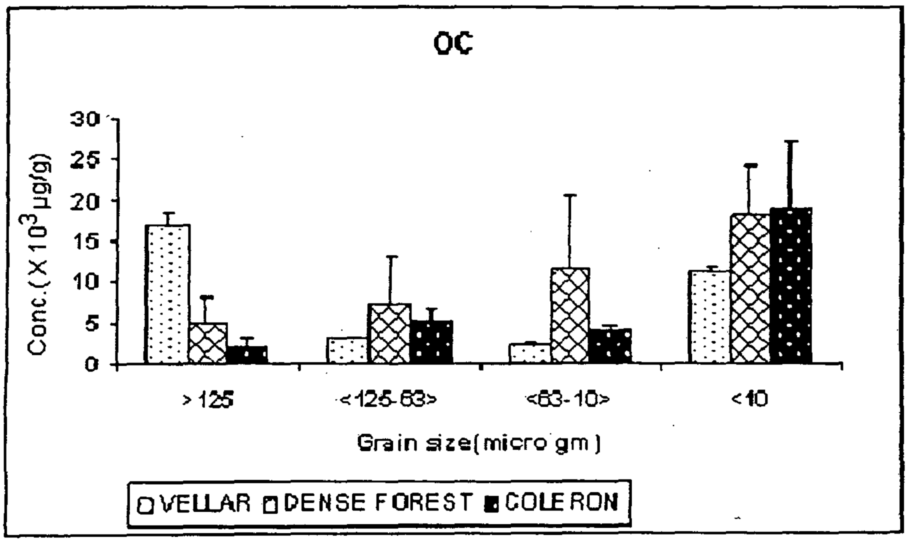


Fig. . 4.11 Variation of Organic Carbon (OC) with grain size in tsunamigenic Pichavaram Sediments



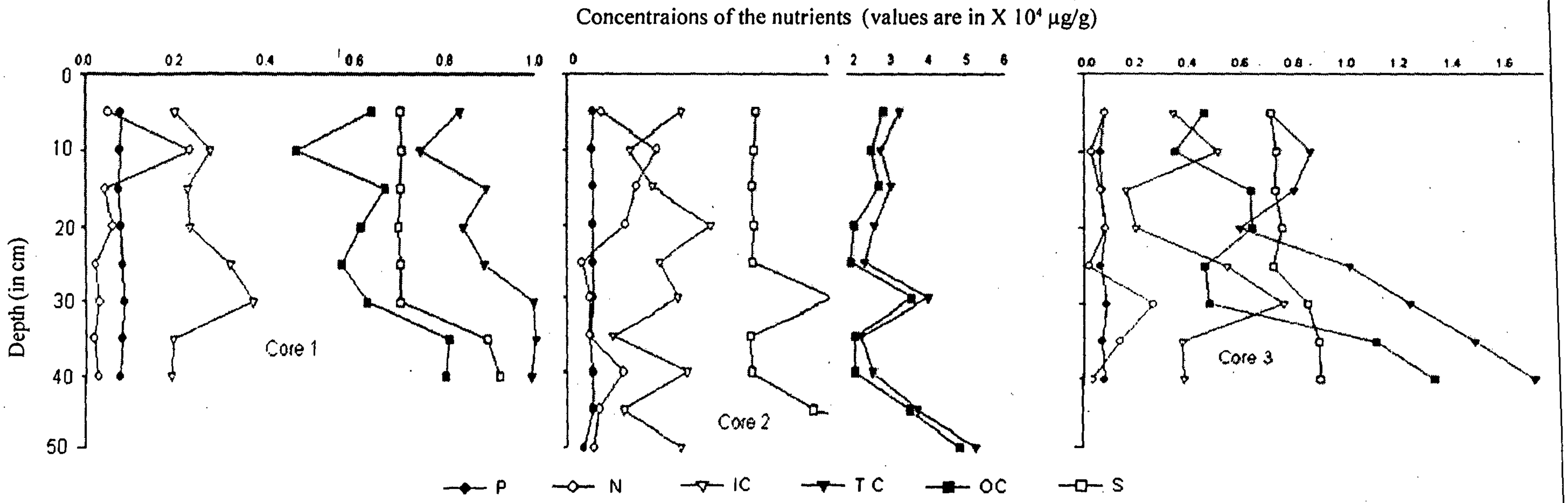
before tsunami was 0.30 X 10^3 µg/g (Prasad, 2005) and it increased to 7.22 X 10^3 µg/g after tsunami. In the core sediments 1, 2 and 3 Sulfur concentration were 6.9 X 10^3 µg/g, 7.1 X 10^3 µg/g and 7.1X 10^3 µg/g found in the surface of the cores respectively. Ramesh et al., (2006) was observed that the sulfur concentration was enriched up to 15 X 10^3 µg/g in the surface sediments to 40 X 10^3 µg/g up to depth of 36 cm in the core sediments in the tsunamigenic sediments of Andaman and Nicobar Islands. In the similar fashion, there was a considerable increase in the total sulfur content of the Pichavaram sediments from 0.30 X 10^3 µg/g (Prasad, 2005) to 7.22 X 10^3 µg/g. High amounts of sedimentary sulfur found in the Pichavaram mangrove sediments might be come on the surface due to the tsunami wave impacts on the burial reduced sediments.

The C/N ratio in the mangrove sediments ranged from 11.45 – 19.59 (Table 4.9). The high C/N values could be due to sediments were poor in nitrogen, which favors net immobilization. The generally high C: N ratio of mangrove (e.g. leaves, wood), high rates of bacterial cell production (Alongi., 1988) and low NH_4^+ flux across the sediment-water interface, (Kristensen et al., 1988) indicate that rates of immobilization may be high in mangrove sediments. Cattle grazing, hyper salinity and other human induced impacts heavily disturbed a large area of the Pichavaram mangrove. The rate of microbial activity was rapid in comparison with rates measured in other mangrove soils, reflecting high rates of phytoplankton production and organic matter retention in Pichavaram. (Alongi et al., 2005) The major losses of nitrogen from the system occur via tidal flushing and, to a lesser extent by the denitrification. Denitrification appears to be very low compared with nitrogen fixation and, as only mid intertidal sediments were examined (Iizumi, 1986) the value (and extrapolation of the rest of the system) is clearly an underestimate. Alongi et al., (2005) observed that carbon and nitrogen concentration was low in the Pichavaram soils compared to other soils, but the molar C: N and N: P ratios are low, suggesting that the labile organic matter is high.

4.3.2 Core Sediment

The vertical distribution of nutrients in the marine hypersaline sediments depends upon the physical forces, pH, temperature and redox potential (Carman et al.,

Fig. 4.12 Variation of Nutrient with depth



1996; Hendricks and White, 2000). A significant variation in the physical factors was observed in all three sediment core samples by increasing the depth. Vertical distribution of the inorganic carbon (IC) and organic carbon (OC) in all three-core sediments of the Pichavaram sediments (pre tsunami and post tsunami) is shown in Fig. 4.12 respectively. It is clear that there was a considerable increase in total carbon and organic carbon with depth. Total carbon and organic carbon concentration was more in core sediments (below 20 cm and onwards) than the surface sediments. In core 2, collected from well inside the mangrove forest, concentration of Total carbon and organic Carbon was higher than the Core 1 and 3, which indicated that mangrove sediments were rich in the organic carbon.

Pre tsunami study showed that there was gradual decrease in nitrogen in the core sediments of the mangroves (Prasad, 2005). This may be due to direct input of nitrate compounds from external sources mainly from the aquaculture effluents, agricultural runoff and domestic sewage. (Purvaja and Ramesh, 2000; Subramanian, 2004) the concentration of nitrogen had increased in all core sediments in tsunamigenic sediments. But there was no any regular variation was observed in the nitrogen and sulfur concentration with depth.

4.4 Phosphorus

The biogeochemical cycling of phosphorus has a multiple compound sedimentary phase (Emsley, 1980) as it can occur in the sediment associated calcium, iron or aluminum or can be precipitated or be adsorbed on the surface of minerals. As an internal source, phosphorus release from the sediment may contribute at an important level as compared with external sources such as atmosphere deposits, agricultural runoff and wastewater discharges (Graneli et al., 1999; Krivtsov et al., 2001). In general, phosphorus concentrations in an aquatic sediments depends on the ecosystem trophic state, sediment composition, sedimentation rate, physico-chemical conditions, iron content and the extent of diagenetic processes (Gonsiorczyk et al., 1998; Frankowski et al., 2002). Rapid degradation of the mangrove forest due to rapid increase in the aquaculture cultivation and other agronomic practices, this certainly supplies considerable amount of P substances to the mangrove ecosystem

Fig. 4.13 Distribution of Phosphorus in different fraction with sampling location

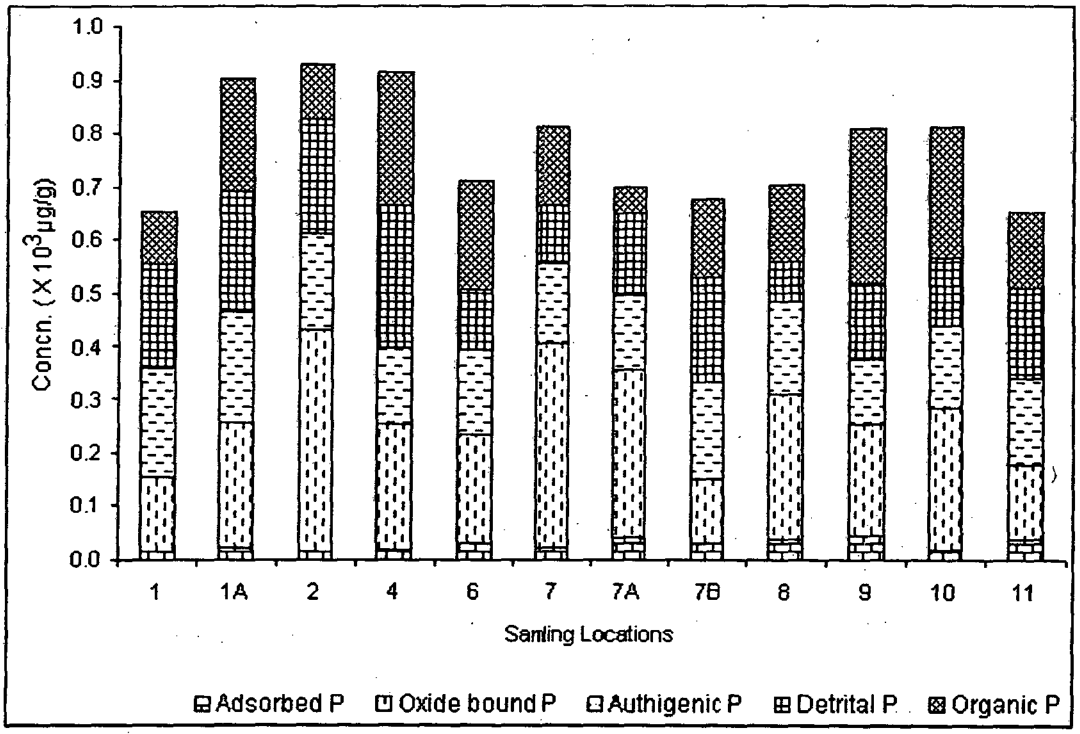
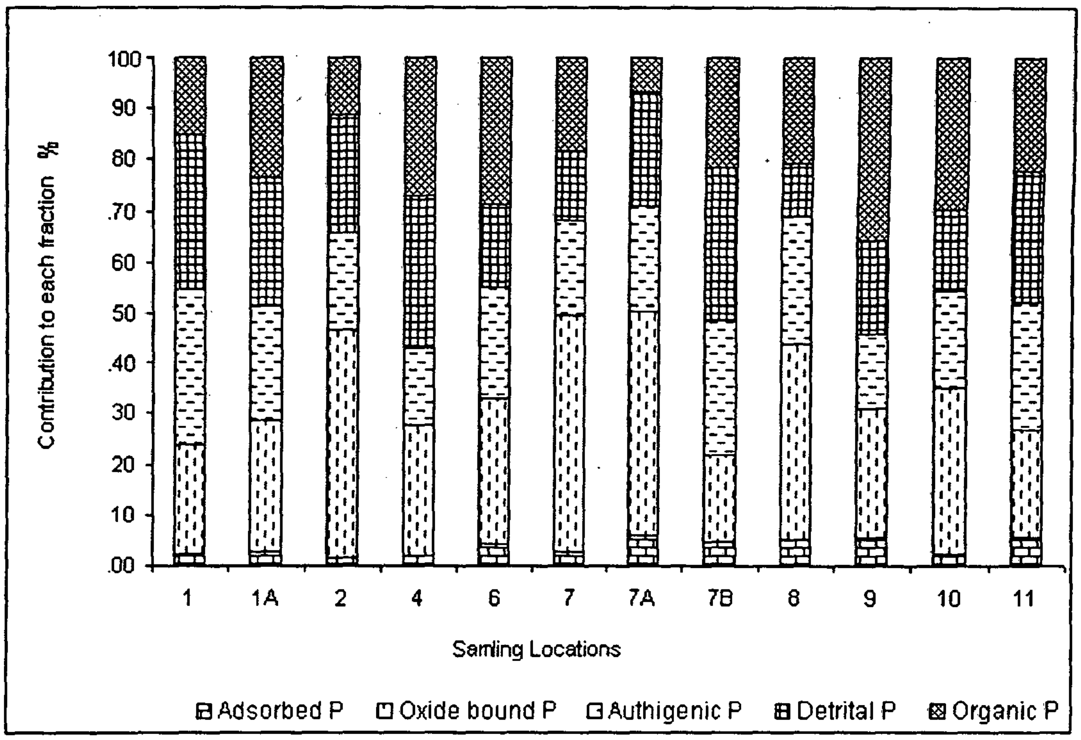


Fig. 4.14 %Contribution of different fraction to total Phosphorus in different fraction sampling location



4.4.1 Phosphorus concentrations in the mangrove sediments

Global average of phosphorus in the mangrove sediments varies between 100 – 1600 µg/g (Alongi et al., 1992). The concentration of Total P in the mangrove sediments was with in the limits of the global average (Table 4.10).Average total phosphorus in the surface sediments was found to be 772 µg/g) in the Pichavaram mangrove sediment. Highest concentration of Total Phosphorus was observed in sample collected at mangrove forest, near Chinnavaikal whereas lowest was sample collected near the mouth of Vellar estuary. The comparison of the ten samples showed that the order of TP concentrations was 2>4>1a>7>10>9>6>8>7a>7b> 11>1. This indicated that sediment collected from the forest area had a considerable amount of total Phosphorus. The grain size distribution showed that forest region had more concentration of finer grain size than adjacent estuary region, as these fine sediments have greater adsorption capacity (Carman and Wulff, 1989; Frankowky and Bolalek, 1970). This was further confirmed by P speciation studies where total TP in the surface sediments is considerably higher indicating that the mangrove sediments had a great potential to supply to the overlying water (Marsden, 1989).

There was no significant vertical variation was observed in all core sediments which may be due to scooping effect of tsunami waves which had disturb the sedimentary redox environment, which is prime regulatory function controlling P distribution in these intertidal sediments (Hendricks and White, 2000). In the Pichavaram mangrove, the sedimentation rate was ranged between 0.4 – 0.7 cm yr^{-1}, this is significantly higher when compared to other lucustrine ecosystems (Ramesh, 2003), and thus the sedimentation rate may be responsible for vertical distribution of P in this mangrove ecosystem. However Prasad (2005) had observed significant vertical variation in the sediment core of the mangrove forest

4.4.2 Speciation of Phosphorus in sediment profiles of the Pichavaram mangrove

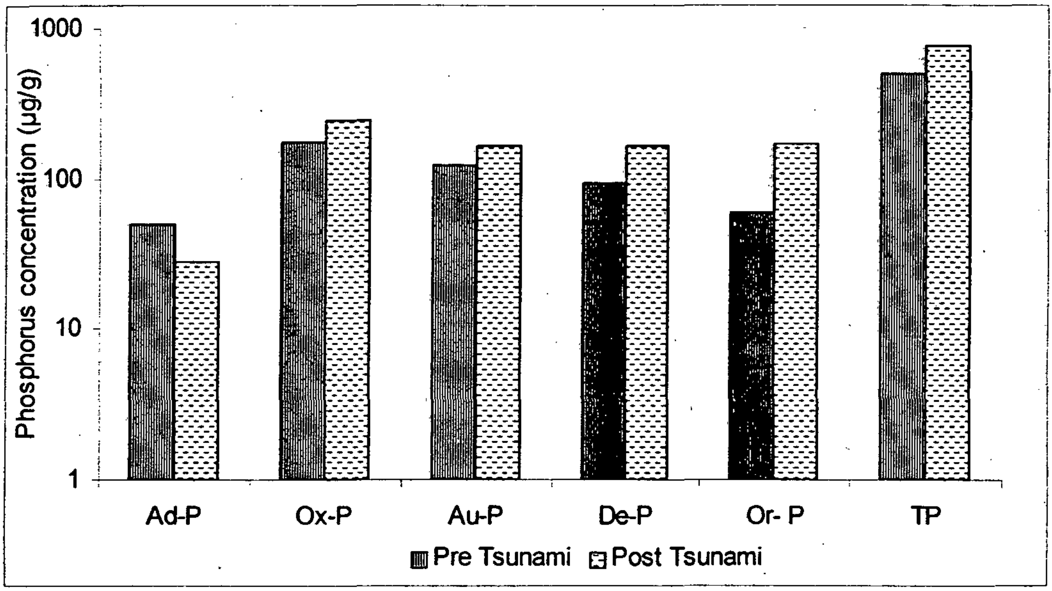
Fig. 4.13 and Fig. 4.14 illustrate the concentration of different P fractions in the surface sediments. The differences among the different fractions of P was statistically tested and found that it was significant at the 95% confidence limits. The mean sediment phosphorus distributions were 27.92 µg/g for adsorbed – P, 243.28

µg/g for oxide bound – P, 165.94 µg/g for authigenic – P, 166.95 µg/g for detrital – P and. 168.78 µg/g for organic – P. The major forms of P and their order of abundance in the surface sediments were: oxide bound -P > organic – P> detrital – P≈ authigenic – P > adsorbed – P whereas in Pre tsunami sediments the major forms of P and their order of abundance in the surfacial sediments were oxide bound –P > authigenic – P> adsorbed – P> detrital – P> organic – P (Ramanathan, 1997; Prasad, 2005)

Study of the different fraction of P in sediments showed that the oxide bound, detritus and organic fractions were more dominant in mangrove areas with vegetation, where as adsorbed and apatite phosphorus was more in Vellar and Coleroon Estuary. Organic fraction was observed to be present significant quantity in the Coleroon estuary as well compared to Vellar estuary. This indicated that contribution from weathering and organic source the mangrove litter to the phosphorus fraction.

Changes in speciation have influenced by the chlorinity variations in the water ways (Ramanathan, 1997). The adsorbed P had decreased in Tsunamigenic sediments. The slightly changed in water pH releases P from the adsorb fraction (Hendricks and White, 2000). Due to mixing of ocean water mixed with the mangrove waters during tsunami, adsorbed P may have released from the sediments. Organic bound fraction was observed more in tsunamigenic sediments which may be derive due to adjoining and aquaculture ponds. Similarly Detrital P was also higher in Tsunamigenic sediments; may be due to the deposition of underlying detritus matter from the estuarine mangroves by the tsunami waves. Detrital apatite, Authegenic $CaCO_3$ and Ferric – Fe bound P were abundant in these regions, influenced by Vellar and Uppanar indicating the contribution from geochemical weathering (Ramanathan, 1997). The Ferric –Fe bound P is invariably present in all the samples due to the natural weathering process and increasing oxidation precipitation of Fe and resulting fixation of P with Fe as ferric phosphate during the deposition of the sedimentary materials (Ramanathan, 1997). The sorption of P to iron may take place in the oxidized surface of sediments or precipitated from overlying water where Fe (III) is more scavenger of P than Fe (II) (Lehtoranta, 2004). Due to tsunami, the sediments interacted with more oxic water (as mention earlier, DO had increased), Fe(II)

*Fig. 4.15 Variation of phosphorus fraction in Pichavarm sediment PreTsunami * and Post Tsunami*



Prasad, 2005

***Table** 4.11 Total phosphorus in the sediments (µ g/g) of the Pichavaram sediments in comparison to other coastal systems*

Study area	**TP**	**Reference**
Pichavaram mangroves-post tsunami	653-901	Present study
Pichavaram mangroves – pre tsunami	357 - 437	Prasad, 2005
Hooghly estuary	258-503	Vaithiyanathan et al., 1993
Sierra Leone mangroves	800 - 1600	Hesse 1962, 1963
Sepetiba Bay	170 - 270	Silva and Mozeto, 1997
French Guina Mangroves	600 - 800	Fabre et al., 1999
Amazon estuary	100 - 270	Silva and Sampaino, 1998
Bohai and Yellow Sea	104 - 199	Liu et al., 2004
Global average	100 - 1600	Alongi et al., 1992

changed into Fe(III), and Fe(III) reacted with P, it might be a cause of increased of Fe bound P in the sediments.

Profile concentrations of various P forms in the sediments from two sampling sites are shown in Figure 4.16. The distribution of P forms in the core strands depends up on the physical forces like pH, temperature and redox state. Oxide bound P fraction is redox sensitive and has been known to be a source for internal P loading (Rydin, 2000). Oxide – P showing conservative behavior in the vertical gradient, where it has been declining rapidly from top to bottom. Organic P the dominant form of all the rest forms and it is showing increasing trend from surface to depth indicating the conservative behavior in both the core. There was no much variation was observed in Authegenic P in core 1.

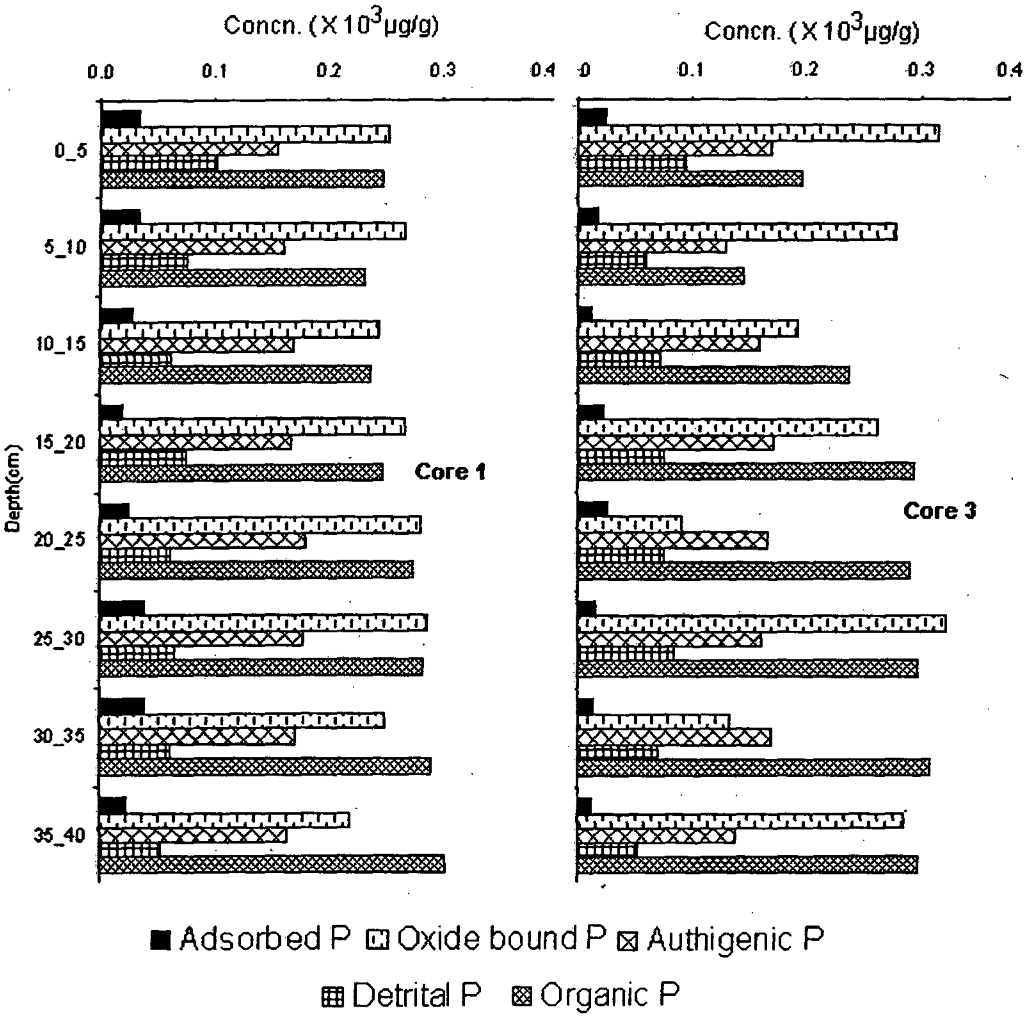
The sequential extraction of phosphorus in the mangrove sediments is an important method to understand the mechanisms controlling the P, whether P is released or bound on the sediment particles (Silva and Sampaino, 1998). The mechanism involved in this processes can be of a chemical or biological nature or a combination of both. The understanding of these mechanisms is used to determine if this element is available to flora and fauna (Jordan et al., 1983; Silva and Mozeto, 1997). Spatial distribution of P fractions in the mangrove sediments were significant and found that absorbed and organic P fractions were increasing towards the interior mangrove region and whereas oxide bound and detrital fractions were increasing towards the mangrove zone. The Authegenic fraction was more dominating in Vellar region than other region. This indicates that around 50 – 60% of P in the Pichavaram sediments were derived from the natural weathering mechanisms, and rest is due to anthropogenic pressure e.g. agricultural runoff and sewage)(Subramanian 2004). The stability of this fraction depends on the pH and phosphate concentration in the natural waters (Golterman, 1988). In the marine systems, the domain of pH and phosphate concentrations was entirely with in the range of precipitated hydroxyapatite, thus it acts as insoluble P reservoir. Any alternations in the ecological function and structure by human disturbances, this trend might have enhanced soluble P form. In case of the Pichavaram mangroves, rapid human interference caused changes in the ecological structure (Alongi et al., 2005) with an effect of converting immobile P phases to mobile P phases. Furthur when the variation phosphorus in the Pre-tsunami (Prasad, 2005) and Post-tsunami sediments were compared, it was observed that difference in Phosphorus in the tsunamigenic sediments indicated that release of secondary phosphorus from the adjoining agricultural zones in the waters.

After tsunami, the concentration of all nutrients including P in water had increased. Existing information on the coastal Fe behavior suggests that Fe is transported as weathered product from freshwater primarily as organically stabilized colloids that are destabilized and flocculated in the low salinity range in the estuarine regions (Sholkovitz, 1976; Boyle et al., 1977). This is attributed to deposition of dissolved Fe from the water column and facilitates adsorption of phosphate on iron oxides, hydroxides and clay, as important processes in marine and fresh water systems (Jensen and Thmdrup, 1993; Slomp et al., 1996). In general organic bound P present in the sediments is considered as unavailable except under reducing conditions (Froelisch, 1988). The formation of P associated with iron oxides in the mangrove sediments has been considered as responsible for the higher phosphate concentrations (D'Elia et al., 1986).

4.4.3 Depth variation of P speciation

P dynamics in the aquatic sediments is controlled by abiotic absorption of P by oxides and biotic microbial metabolism (Enell and Lofgren, 1988; Davelaar, 1993). The relative variation of different fraction in depth may be influenced by the tidal inundation which influences the chemical reactions involved in the retention and release of P in the sediment. On an average there was no significant changed in the absorbed P was observed in the core sediments up to 40 cm. in the tsunamigenic sediments. Oxide bound fraction was dominant than organic bound P in both core. There was not consistent variation of Fe -oxide bound phosphorus was observed into the tsunamigenic core sediments. The relative vertical abundance of oxide bound P in the depth is a function of pH (Hendricks and White, 2000). As pH decreases, the surface charge of solids changes, and the adsorption of phosphate to iron, aluminum and some other clays increases (Enell and Lofgren, 1988). Fe – oxides can adsorb PO_4 – P in stoichiometric ratios (Fe: PO_4) ranging from 2 – 40 (Jenssen et al., 1992; Griffioen, 1994) depending upon pH and redox conditions. After tsunami the tsunami

Fig. 4.16 Variation of P fractions with depth



waves disturbed the pH of water, this might lead to the changes in adsorbed and Fe-oxide P were observed in the tsunamigenic sediments. As in core 1 (Vellar estuary region), the tsunamigenic sediments deposited goes up to 90 cm where as Core 3 (Pichavaram mangrove region) deposits reached upto 25-65 cm.(Seralathan et al., 2006).

Organic bound P had increased with depth in the tsunamigenic sediments. In core sediment with depth, oxic condition changes into sub-oxic and finally anoxic. This results in lower redox potential causing P to desorbs from solids and return to the solution. This P might have absorbed by the organic matter, mainly from humic substances and will be available as nutrients source for the reducing bacteria. Thus at the deeper layers organic bound P was higher in both sediments. This high organic P was observed in the tsunamigenic sediments was also might be due to newly deposits sediments mixed with retreating sediments with agricultural run off from the adjoining area.

Adsorbed –P showed an identical behaviour in sediments with depth. Due to change in pH of the water column, the adsorbed-P has been found less than previously reported values (Prasad. 2005). Due to change in oxidizing environment as a result of tsunami, the oxic condition would promote to desorb from the sediment particle and will be available to the biological system. The upper layer (0-10 cm) showed more oxide bound phosphorus owing to stability formation of FeOOH-P complexes (Lehtoranta, 2004). The relative vertical abundance oxide bound-P in the vertical profile is a function of pH (Hendricks and White,2000). With decrease in pH , there is change in surface charge of solids, thus increasing the adsorption of phosphate to iron, aluminum and some clay increases (Enell and Lofgren, 1988) The decrease in the organic-P is due to the conversion.

In the lower region, the increase in organic phosphorus is mainly due to reducing environment (lower redox potential) causing P to desorb from solids and return to the solution. This fraction might have absorbed by the organic matter mainly humic substances and will be available as nutrient source for the reducing bacteria (Prasad, 2005). Thus at the deeper layers organic bound P was higher in core sediment.

There was no trend observed in case of authigenic and detrital–P with the depth which may be attributed to the complex mangrove variability of phosphorus (Ramanathan, 1997).

4.4.4 Release potential of sediment P

The actual release of P from the mangrove sediments is governed not only by the ecosystem reservoir of exchangeable P, but also by the other factor such as pH, redox conditions and bioturbation (Hendricks and White, 2000; Alongi 1998). After tsunami pH had slightly increased in the water column, resulting in increased salinity, the pH value in this mangrove system has increased with time (Subramanian, 2004). These processes influence the pH of sediment–water interface; as a result this change in pH could accelerate the release of oxide bound P to the overlying water. Also the total phosphorus in tsunamigenic sediments had increased by ≈ 56%. As a whole, P released from the sediment is supplying P for the development of algae in water. If this has continued for next few years, algal blooms, will in turn, increase the pH of mangrove water, and degradation of dead algae decreases the Eh value at the sediment–water interface and increases P concentrations in surface sediments, which would accelerate the P release. The release of phosphorus and appearance of the algal bloom would stimulate reciprocally, which may result in self-fueling. This will become potential reason for degradation of water quality in the Pichavaram mangrove in near future, in addition to, reduction in the fresh water input, which certainly results in decrease of biodiversity. Therefore, sediment internal load should be taken into account in future for restoration of the ecologically sustainable coastal wetlands like this mangrove ecosystems.

4.5 Behaviour of Silica and Alumina in Tsunamigenic Sediments of Pichavaram

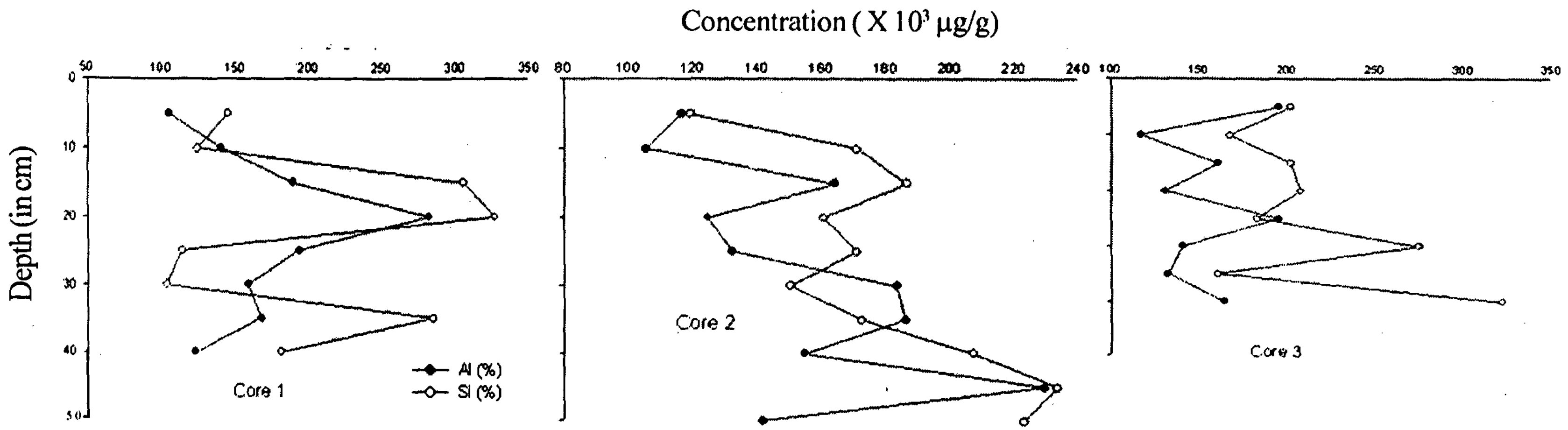
The Silicon concentrations in the tsunamigenic sediments were more or less uniform and entire region indicated that the presence of uniform quartz content. The variation in Si /Al ratio indicated that these variations may be due to variation in quartz content in the sediments (Calvert et al., 1993). The mean concentration of Si in the tsunamigenic sediments was found 243±33.95 x 10^3 µg/g whereas the concentration of Si in pre tsunami surface sediments was 340 x 10^3 µg/g (Ramanathan et al., 1999). The texture of tsunamigenic sediments is dominant in the fine silt and clay, hence the Si concentration was found less than the previous studies by Ramanathan et al., 1999. Ramanathan et al., 1993, observed that increase in chlorinity after intense tidal mixing would decrease the Si concentration in estuarine sediments. As during tsunami the sediments came into the contact with chloride rich seawater, thus lowering the concentration of Si (Fig. 4.17). Seralathan et al., (2006) observed that in tsunami affected area of Tamil Nadu coast, the percentage of clay and silt content had increased from 2.34 to 6.7 %. Such enhancement was due to the admixture of fine sediments brought forward by the receding tsunami waves from the hinterland with high alkalinity.

Grain size data showed that the Si concentration was dominant in grain size > 63-µm size. The Vellar region shows the high concentration of Si than other region. In this context, it is important to note that quartz was the dominant mineral species present in the Vellar and Coleroon region with high pH environment (Ramanathan et al., 1999).

The percentage of Al concentration after tsunami varies from 13 to 21 % with mean as 18 %, where as before tsunami it ranges from 13% to 25% with 18% as average concentration. Thus it can be concluded that tsunami had no significant impact on aluminum concentration.

The mean concentration of Al was in the tsunamigenic sediments were found 195±38.87 x 10^3 µg/g. whereas the concentration Al pre tsunami surface sediments was 176 x 10^3 µg/g (Ramanathan et al., 1999). The increased in Al concentration was due to the changed into texture of the tsunamigenic sediments from medium – fine sediments to fine - very fine sediments and dominance of clay into the sediments. The grain size data showed Al concentration was found approximately equal in all grain size > 10 µm, but maximum concentration was

Figure 4.17 Variation of Silicon and Aluminum with depth



observed in < 10-μm-size fraction. Along with this increase of Al was significantly due to tidal mixing, adsorption –desorption, and flocculation process (Ramanathan et al., 1993).

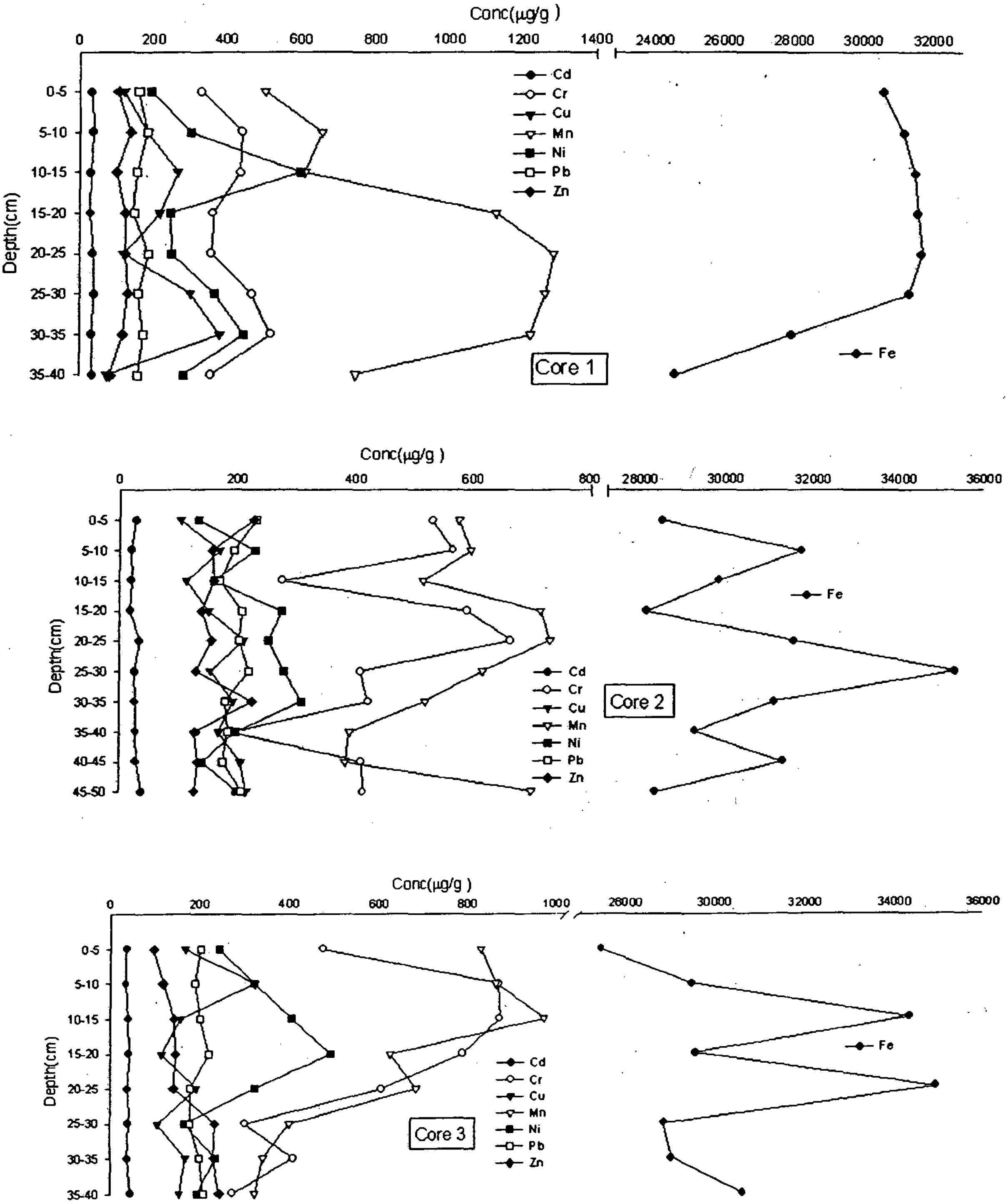
4.6 Behaviour of Heavy Metals in Tsunamigenic Sediments of Pichavaram

Mangrove sediments are anaerobic and reduced, as well as being rich in sulphide and organic matter (Silva et al., 1990). They, therefore, favor the retention of water-borne heavy metals and the subsequent oxidation of sulphides between tides allows metal mobilization and bioavailability (Silva et al., 1990; Tam and Wong, 2000). Concentrations of heavy metals in sediments usually exceed those of the overlying water by 3–5 orders of magnitude (Zabetoglou et al., 2002) and, with such high concentrations, the bioavailability of even a minute fraction of the total sediment metal content assumes considerable importance with respect to bioaccumulation within both animal and plant species living in the mangrove environment. Since heavy metals cannot be degraded biologically, they are slowly transferred and concentrated into plant tissues from soils and pose long-term damaging effects on plants. After decomposition of mangrove leaves, it ultimately reaches to mangrove sediment. Tam and Wong (1993), suggested that the mangrove soil component has a large capacity to retain heavy metals, and the role of mangrove plants in retaining metals will depend on plant age and their biomass production.

4.6.1 Total heavy metal concentration in tsunamigenic Pichavaram mangrove Sediments

The recent tsunami sediments are similar to depositional effects of the others reported earthquake-generated tsunami waves (Dawson et al., 1996; Dawson and Shi 2000; Gelfenbaum and Jae 2003; Szczucinski et al., 2005). Heavy metals in the tsunamigenic sediments of the Pichavaram were compared with the heavy metal concentrations reported by Ramanathan et al., (1993). The observed enrichment of the heavy metals may be explained by the unique chemical behavior of the mangrove sediments.

Figure 4.18 Variation of heavy metals with depth



The mangrove sediments acted as a trap for many toxic metals including Zn, Cr, Ni and Cu. However, at certain sites, interior mangrove creek, the sediments at Upannar zone showed more concentration than the other sites. The higher concentrations were patchy and vary from one metal to another, which may be attributed to the complex nature of mangrove sediments (Ramanathan et al., 1993; Badarudeen et al., 1996). Overall, there was a significant increase in the concentration of some of the metals in the tsunamigenic surfacial sediments and core sediments as compared to previous studies (Ramanathan et al., 1993, 1999.) Seralathan et al., (2006) observed that tsunamigenic sediments collected near Pichavaram and adjacent areas Devanpattnam, Sothikkupam and Muthukkuthurai contained abundant heavy minerals than the pre-tsunami sediments.

Heavy metals are categorized into two groups based on the changes in concentration due to tsunami (Fig.. 4.22-4.29). The first includes Cd, Cu, Cr, Pb, and Ni, whose concentrations are higher in tsunamigenic sediments than the previous studies (Ramanathan et al., 1999). In the second group, Fe, Zn, and Mn, as there is less variation or decrease as compared to the sediments studied before tsunami (Ramanathan et al., 1999). Similar results were observed by Szczucinski et al., (2005); Ramesh et al., (2006); Prasad et al., (2006); during study of the impact of tsunami on the sediments of different areas.Thus our study reveal that the heavy metal associated with heavy minerals were brought by tsunami into the mangrove from the shelf zone.

4.6.1.1 Cadmium (Cd)

The mean concentration of Cd was found 32.03 µg /g. The minimum concentration of Cd was 13 µg /g in Coleroon estuary and maximum concentration was 41.77 µg /g in dense mangrove forest. Cd concentration near Khan shahib Canal was highest which indicates that surface sediments are extremely contaminated, most probably as a result of synergistic effect of anthropogenic activities, fertilizers which was driven by Vellar, Uppanar and Coleroon river and the tsunami driven sediments from the deep ocean.

The mean value of Cd concentration in pre-tsunami sediments was reported to 6.96 µg /g (Ramanathan et al., 1999, Subramanian 1990). After tsunami, Cd concentration had increased by 5-6 times. The average cadmium concentration in the earth's crust varies between 0.1 and 0.5 µg /g. High levels of Cd accumulate in sedimentary rocks, and marine phosphates and phosphorites have been reported to contain levels as high as 500 µg /g (Cook and Morrow 1995, WHO 1992). So, the increase in Cd concentration can be attributed to fact that marine sediments from deep oceans, which are rich in Cd, are trapped in mangrove sediments after the tsunami and thus results in such a manifold increase in its concentration. Similar observation of increase in Cd concentration is also observed in Thailand where the mean concentration of Cd was increased up to 1.2 μg /g (0.6-1.7 μg /g) after tsunami whereas the reference sample had Cd concentration 0.1 μg /g, which was12 times higher than the before tsunami (Szczucinski et al., 2005).

Grain size analysis showed that maximum concentration of Cd was present in <125-63> μ size, whereas samples from Vellar estuary shows the maximum concentration was present in <63-10> μ size particles. In samples from Coleroon estuary, the maximum concentration was found in >125 μ and <10 μ size. In all core, concentration of Cd with depth was more or less remained constant.The finer grain size rich in clays and organic matter enhance the Cd concentration (Fig. 4.19, 4.20).

4.6.1.2 Chromium (Cr)

The mean concentration of Cr in pre tsunami Pichavaram mangrove was 110.12 μg/g (Ramanathan et al., 1999). The Cr concentration after tsunami varies from 286 to 885 μg/g with mean concentration 589 μg /g.

There was unusual higher value of chromium concentration found in all samples. The river mouth sediments show a sudden increase of metal concentrations compared to inter-riverine coastal sediments (Subramanian and Mohanchandran, 1990). It has been reported by Seralathan et al., (2006) that considerable amounts of heavy minerals carried by tsunami waves from the continental waters in which garnet family is dominant, in this uvarovite {$Ca_3Cr_2(SiO_4)_3$} is the major form which might contribute Cr after Tsunami. Since heavy minerals containing Cr is more, Cr concentration had increased in the mangrove sediments due to tsunami impact from the shelf zone. Besides these, there are several industries in vicinity of Uppanar estuary which releases its untreated effluent discharge directly into water, could also be cause for higher Cr concentration (Khan et al 2004). The fishing harbour near Vellar estuary also contributed Cr into mangrove water and sediment due to oil spill (Schumacher et al., 2001). In core 1 the Cr concentration was observed least where as core 3 it was highest. In all core Cr concentration was decreasing with the depth. The higher Cr is observed in interior channels (Fig..4.18).

Fig. 4.19 Variation of metals in grain size

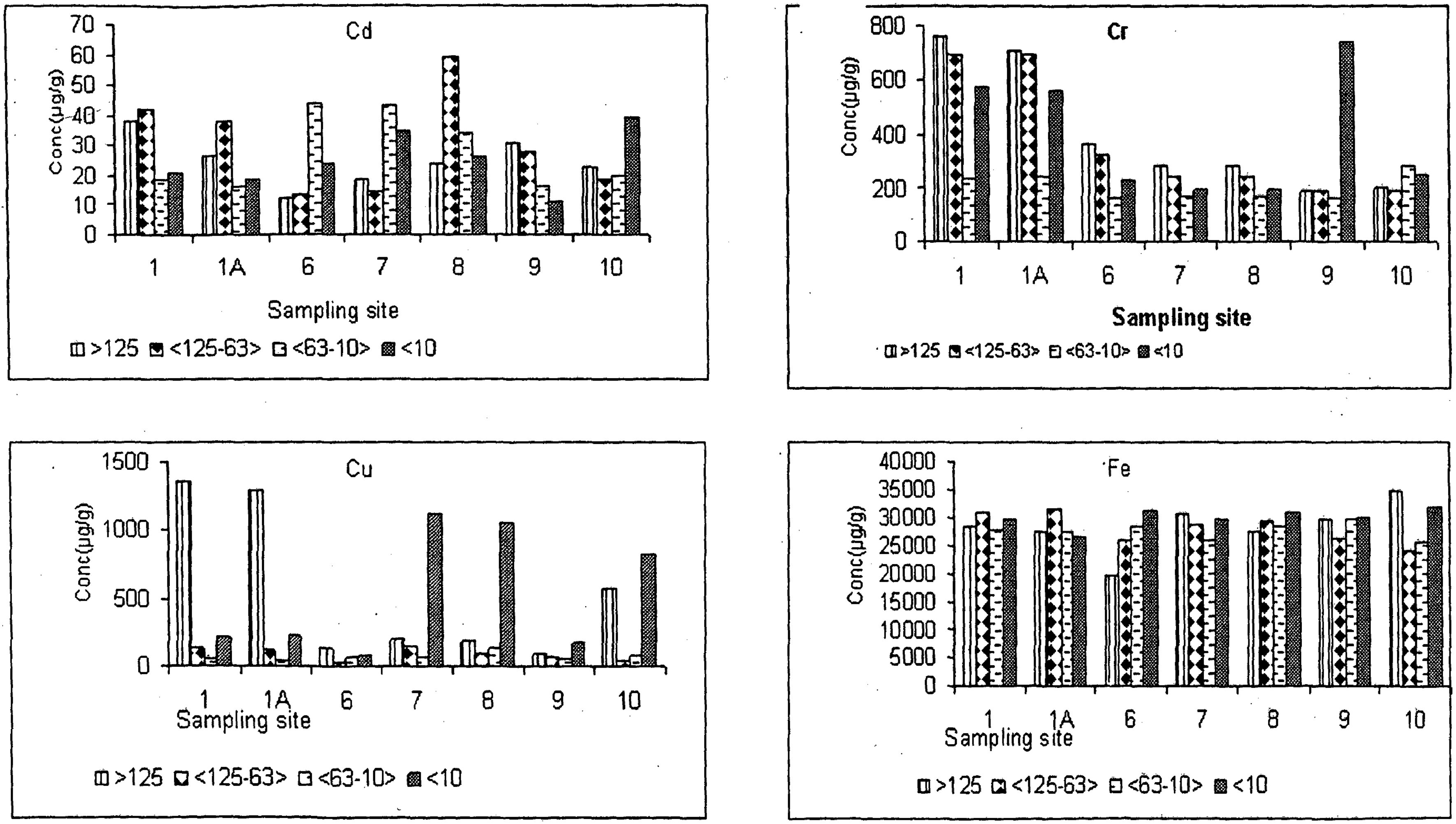


Fig. 4.19A Variation of metals in grain size

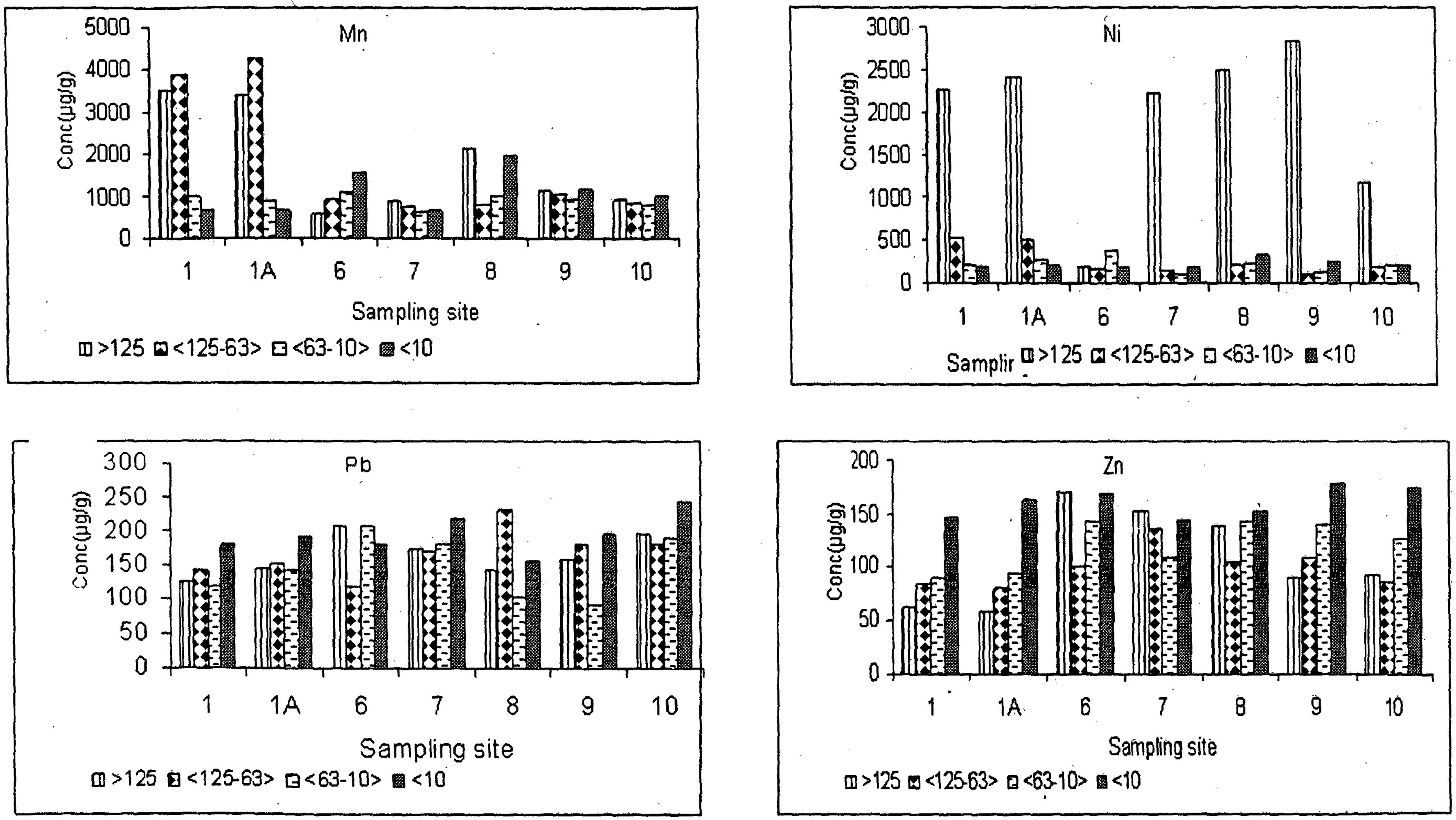


Fig. 4.20 Zonal Variation of metals in grain size

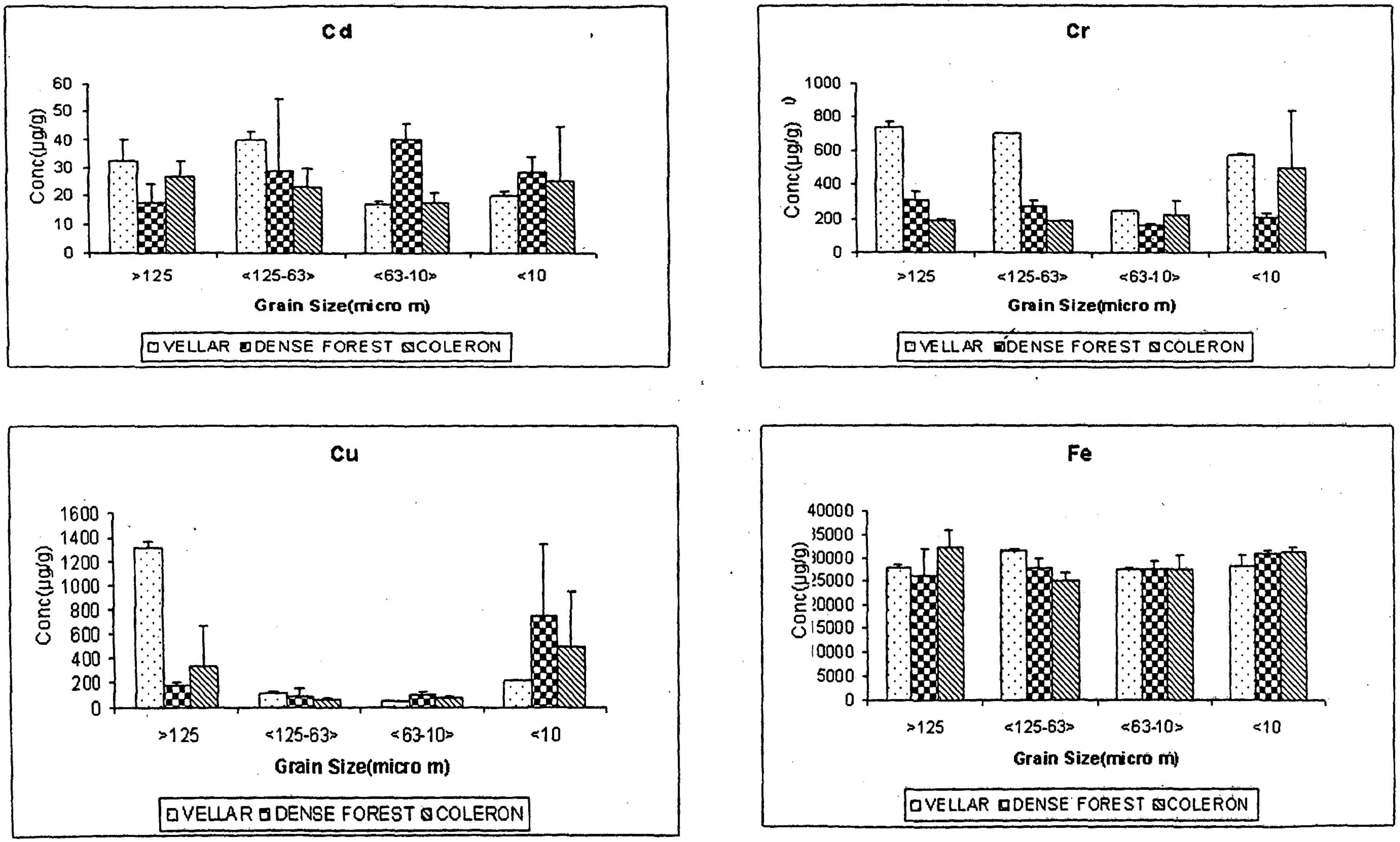
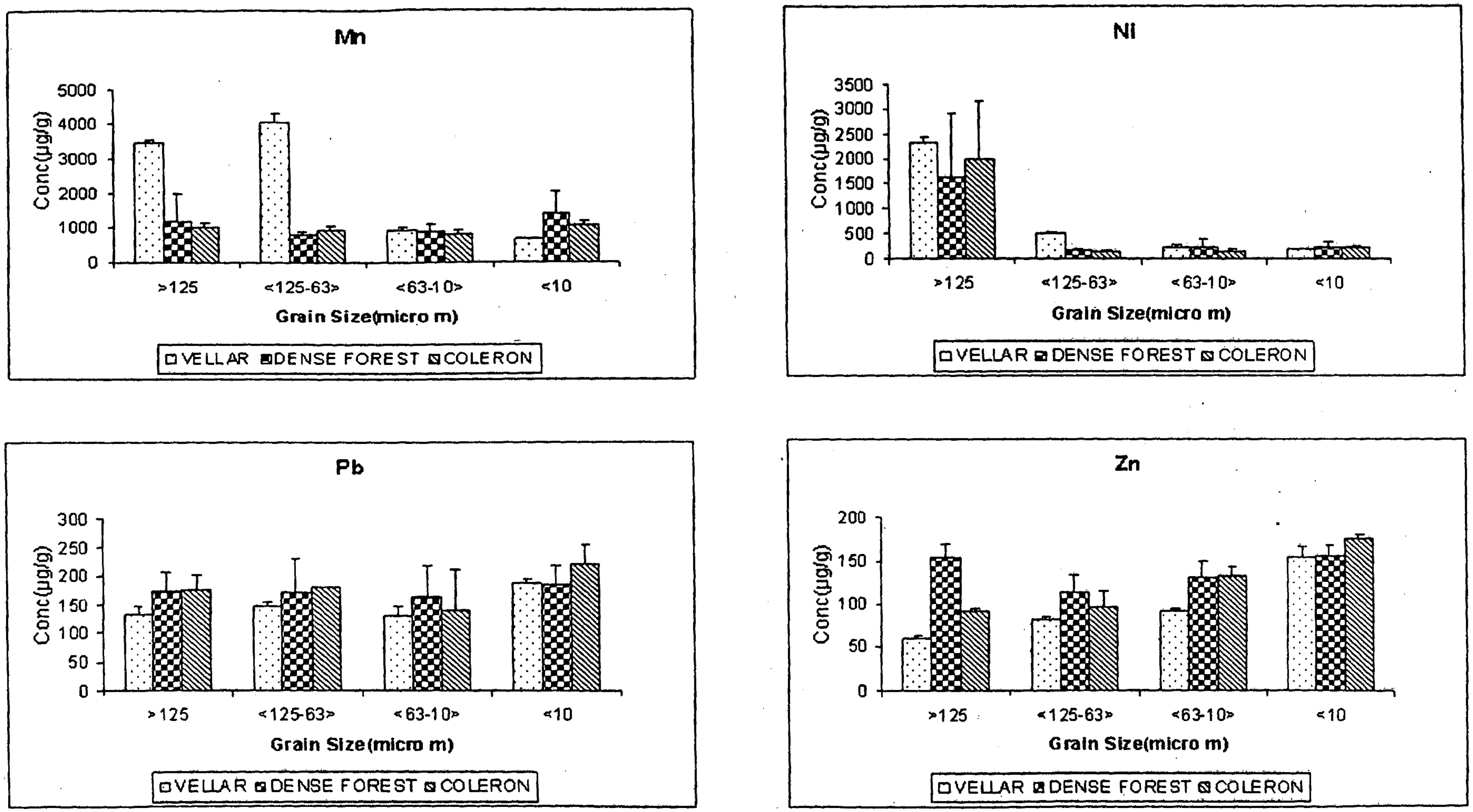


Fig. 4.20A Zonal Variation of metals in grain size



4.6.1.3 Copper (Cu)

The mean concentration was observed as 146 µg /g whereas the minimum value was 88 µg /g (sample 1) and maximum was 267 µg /g (sample no 4). The contour showed in Vellar estuary area was less concentration than the Coleroon river estuary. The Cu concentration in pre-tsunami sediments was 32 µg /g (Ramanathan et al., 1999), after tsunami there is an significant increase in the Cu concentration and is high in nearly all the samples. The high Cu is either derived from the estuarine sediment or from the agricultural soils brought back by Tsunami waves.

In all sediment core samples, Cu concentration had decreased with the depth. Grain size analysis showed that Cu concentration was more dominated in >125 µm in Vellar zone, whereas in Coleroon and Pichavaram zone its concentration was dominated in < 10 µm grain size. (Fig. 4.19, 4.20)

4.6.1.4 Iron (Fe)

In the surfacial sediments, the mean concentration of iron (Fe) was found to be highest 25,500 µg/g, as compared with rest of heavy metals. Before tsunami the Fe concentration was 29,940 µg/g (Ramanathan et al., 1999), this decrease may be due to desorption process after tsunami as well as since the prime source of iron is weathering and formation of dam over Coleroon river has checked the fresh water inflow in the mangrove estuarine complexes, thus resulting the decrease concentration of iron in sediments Hence there is decrease in Iron concentration in surfacial sediment due to tsunami.

Fe is the dominant heavy metal in the core sediment of the Pichavaram. Fe concentration was found minimum at the top and increased with depth upto 30 cm and then decreased in bottom **(Fig. 4.18)**. However, core 2 and 3 showing irregular trend in Fe distribution. This indicate the complex processes occurring in mangrove sediment due to change in redox of the sediment before and after tsunami.When the distribution of Iron in the different size fraction was considered it was observed that maximum concentration of Fe was present in > 125 µ in samples 7, and 10, whereas in sample 6,8, 9 and 1 the maximum concentration was present in <10 µ and 125-63 µ size particle respectively. After tsunami the silt hold more iron due to dominance of heavy minerals (Fig. 4.19, 4.20).

4.6.1.5 Manganese (Mn)

The Manganese (Mn) concentration in the present study varies from 425 µg/g to 1513 µg/g, with mean concentration of 914 µg/g. Before tsunami, it ranges from 86 µg/g to 1900 µg/g, with mean concentration as 701µg/g. Thus, we can infer a slight increase in Mn Concentration after tsunami.

In core 1, the Mn concentration was increased from the top (501 µg/g) to the depth of 20-25 cm (1284 µg /g) and then decreased (Fig. 4.18). In the core 2 and 3 are also showing approximately similar trend of core 1. Grain size analysis showed that maximum concentration of Mn was present in <10 µ in samples 6,9 and 10 whereas in sample 7 and 8 maximum concentration was present in >125 µ size particles(Fig. 4.19A, 4.20A).

4.1.6.6 Nickel (Ni)

There was also a significance change in Ni concentration in the study area after tsunami indicating the lesser contribution of Ni for heavy minerals. But the effluent discharge from nearby chemical industries could be a potential source for Ni contamination in mangrove sediments (Khan 2004). The mean concentration of Ni in present study is 231 µg /g .The minimum concentration observed is 91 µg /g is in Vellar region and maximum 567 µg /g in Coleroon estuary where as earlier reported Ni concentration in this area was 38-86 µg /g (Ramanathan, 1997).

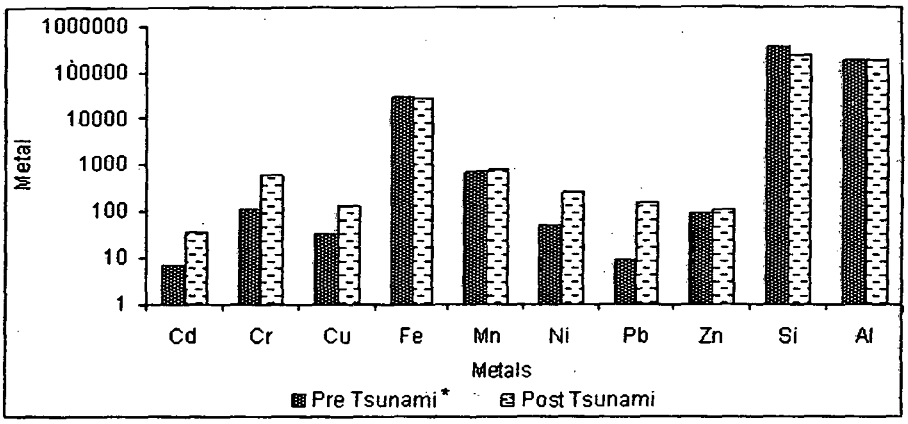
Ni showed a very good correlation with Cr, Cd and Fe in surfacial sediments. Grain size analysis showed that maximum concentration of Ni was present in >125 µ in samples in most of samples (Fig. 4.19A, 4.20A)

In the all core the Ni concentration were decreasing with depth. But in core 3, the Ni concentration was increasing with 20 cm depth, after that its concentration had decreased. As Ni was more dominated in >125 µm grain size it might be due to controlled by coarse grain size fraction up to depth of 20 cm(Fig. 4.19A, 4.20A).

4.6.1.7 Lead (Pb)

Pb was also found in high concentration in all samples. Its mean concentration was 145 µg /g and minimum concentration as 103 and maximum values was 183 µg /g. Its concentration was found higher in Vellar estuary area, MGR Tittu area, and Chinavaikal area than the central forest area (near Upnnar river area) and the Coleron river area. The high value of Pb concentration in tsunami affected area; there were two possible

Fig. 4.21 Changes in the elemental concentration after Tsunami



(Ramanathan et al., 1999)*

explanations given by Szczucinski et al., (2005). One is that the seawater translated on land with the tsunami wave had distinctly different Pb concentrations than the average seawater. The second possibility is that high amounts of litho- or anthropogenic Pb was released during the event and was tied with salt compounds mainly. In this context the Pb concentration increased may be due to direct input of nitrate compounds from external sources mainly from the aquaculture effluents, agricultural runoff and domestic sewage (Purvaja and Ramesh, 2000; Subramanian 2004). Further, the Negative correlation of Pb with the all elements and organic matter suggests that source of this Pb might be come from the inundated tsunamigenic sediments brought back after leading into agricultural and aquaculture sources.

Grain size analysis showed that Pb was present in all fraction of grain size, but predominant in > 10 μm in samples from Vellar and Coleroon region, whereas in dense mangrove forest region, the maximum concentration was present in >125 μ and .125-63 μ size particle respectively(Fig. 4.19A, 4.20A).. Pb was also decreasing with depth in all core sediments.

4.6.1.8 Zinc (Zn)

The minimum Zn concentration after tsunami was observed as 72 μg/gm with maximum concentration up to 140 μg/gm with mean concentration of 103 μg/gm. Before tsunami, the Zn concentration was reported as 89 μg/gm (Ramanathan et al., 1999), not much significant change in Zinc concentration after tsunami.

The concentration of Zn was higher in central region than the other region. In all cores, distribution of Zn was almost constant from top to bottom (Fig. 4.18). However, higher concentration of Zn was found in core 2. In the middle, Zn showed higher concentration, this may be because of re-oxidation probably leads to heavy metal being released in the dissolved phase and loss of carbonate. And depending upon the kinetics heavy metal increased in the middle part, probably due to it was rapidly precipitated with Fe- oxy hydroxides (Marchand et al., 2006). Grain size analysis showed that maximum concentration of Zn was present in >250 µ in samples 6, and 7, whereas in sample 1, 8, 9 and 10 maximum concentration was present in <10 µ size particles(Fig. 4.19A, 4.20A). All the core sediment showed lower concentration in the top few cm and shows increasing trend in the middle layer and decrease in the deeper zone. This indicate the impact of Tsunami on the top and middle layer followed by post depositional change and bioturbation adding heavy metal to biota and deeper layer.

There is not much change in metal concentration in the surface sediments after Tsunami except for Cr, Cd, Cu, Ni, Pb, Zn indicating the enrichment of the heavy metals by heavy minerals brought by tsunami water from shelf region and from the adjoining agriculture and aquaculture.

4.6.2 Spatial variation of metals

The spatial variation of metals given in (Fig.. 4.22-4.29) from this it is clear that tsunami sediments have contaminated due to heavy metal which are mainly derived from adjacent terrestrial places and Uppanar river have supplied higher load of effluents to Pichavaram mangroves. These sediments contaminated by both natural (tsunami) and anthropogenic activities like agriculture and aquaculture and landuse changes (Fig.. 1.4, 3.1).

When the contour maps of Cd and Cr (Pre tsunami and post tsunami) were compared it was observed that concentration in estuarine complex has increased drastically with areas dominated by mangrove vegetation. This indicates that mangrove sediment act as trap for these heavy metals (Lacerda et al., 1998).

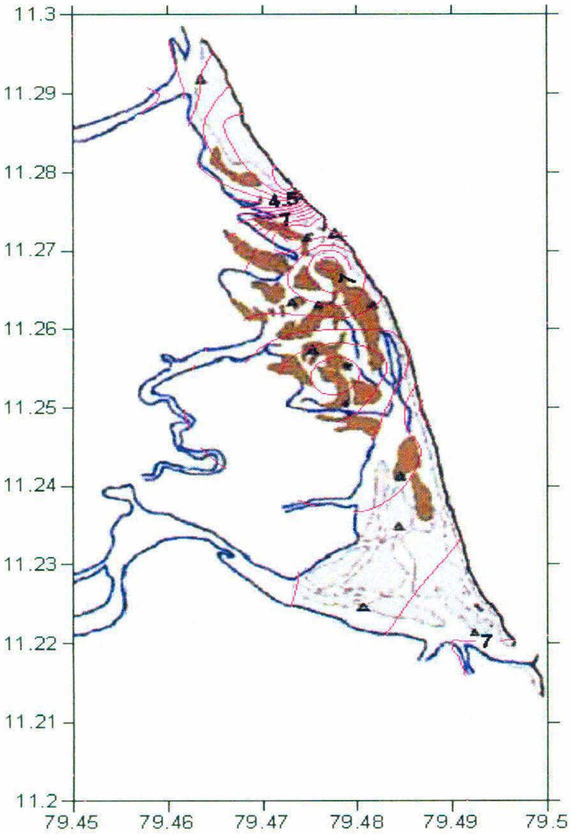


Fig 4.22 Contour map of Cd (Pre-Tsunami)

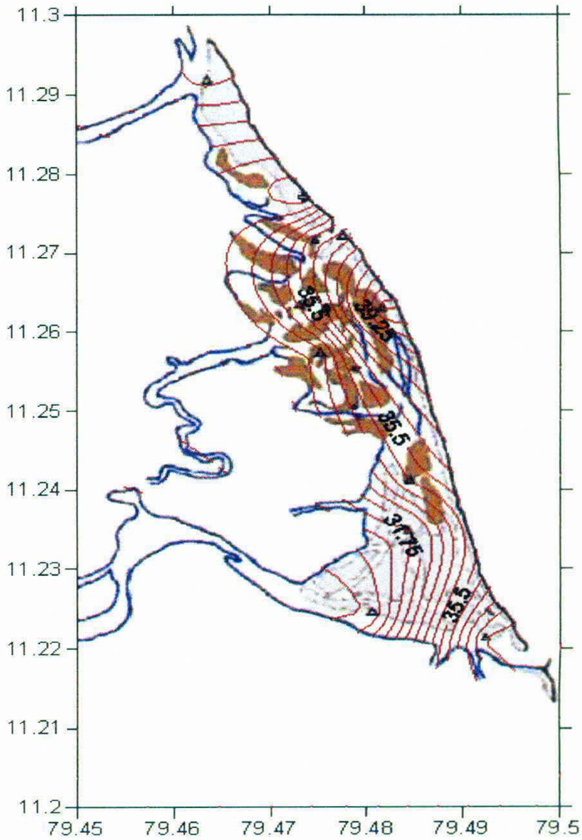


Fig. 4.22A Contour map of Cd (Post-Tsunami)

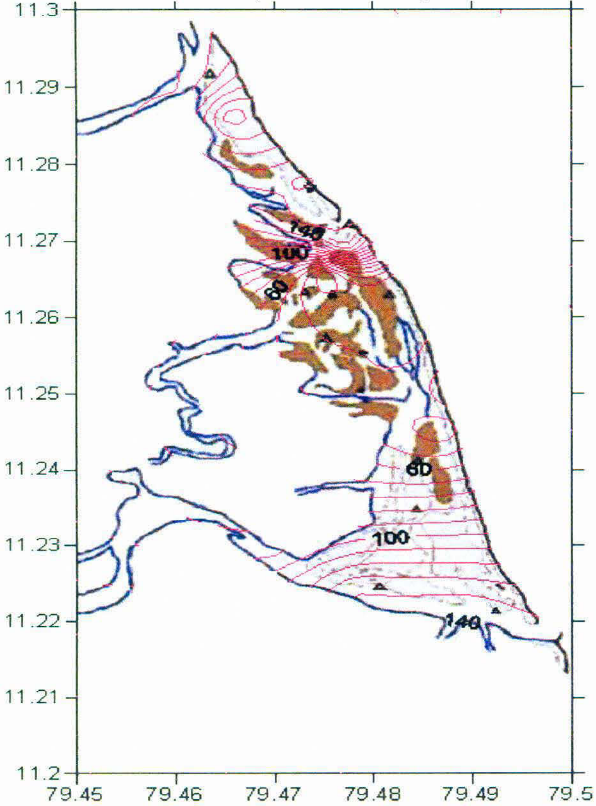


Fig. 4.23 Contour map of Cr (Pre-Tsunami)

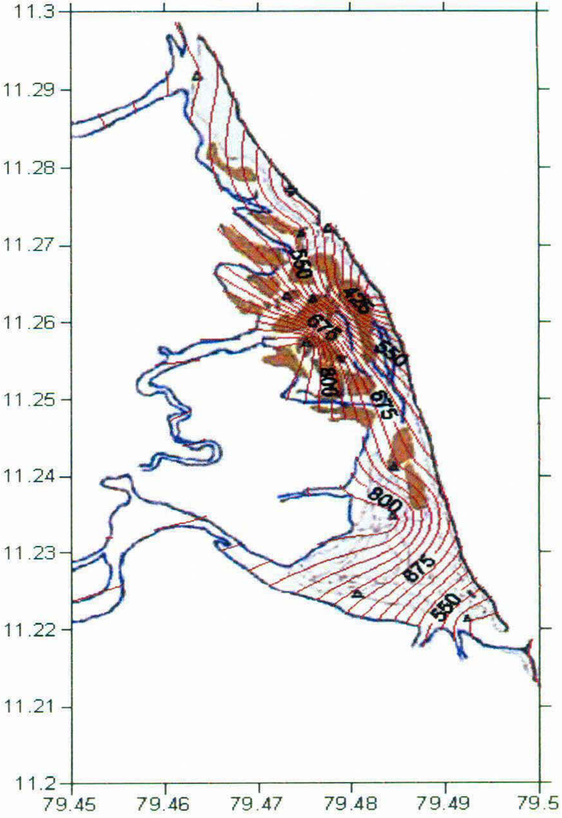


Fig. 4.23A Contour map of Cr (Post-Tsunami)

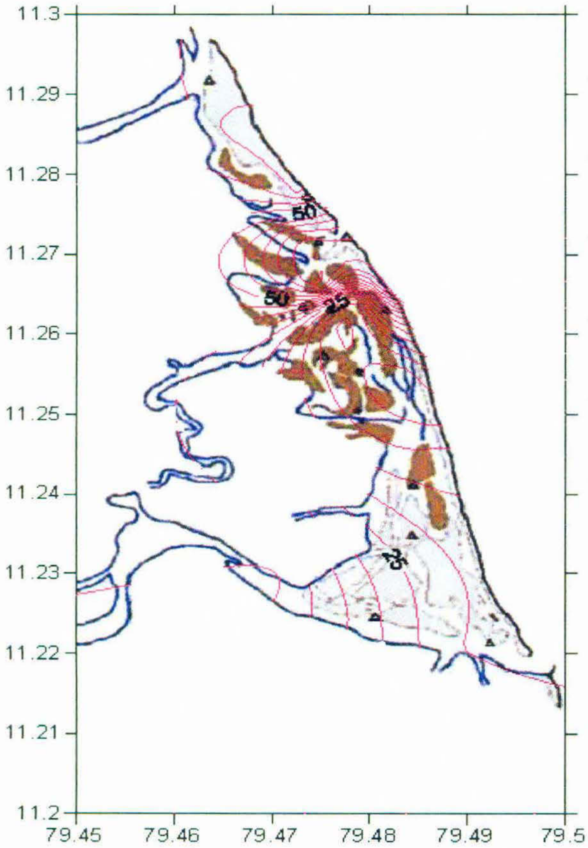


Fig 4.24 Contour map of Cu (Pre-Tsunami)

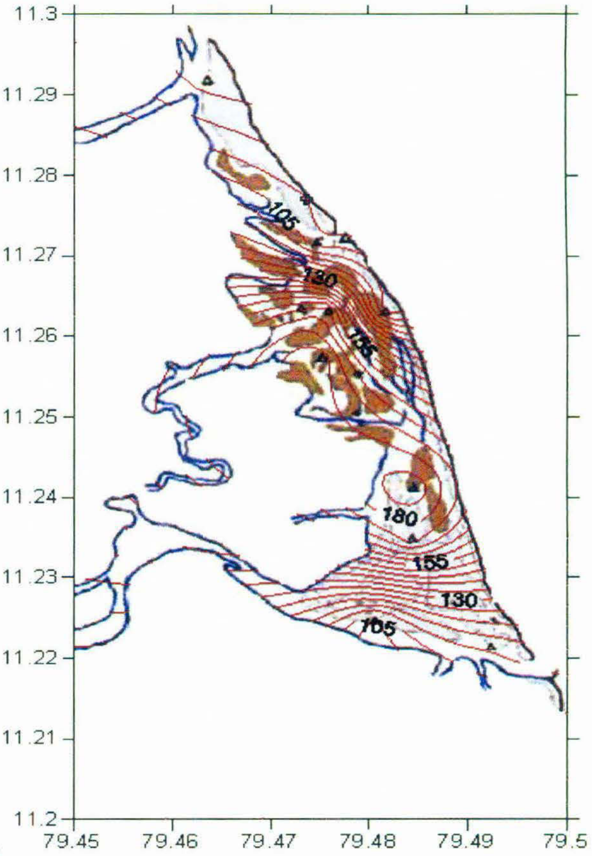


Fig. 4.24 A Contour map of Cu (Post-Tsunami)

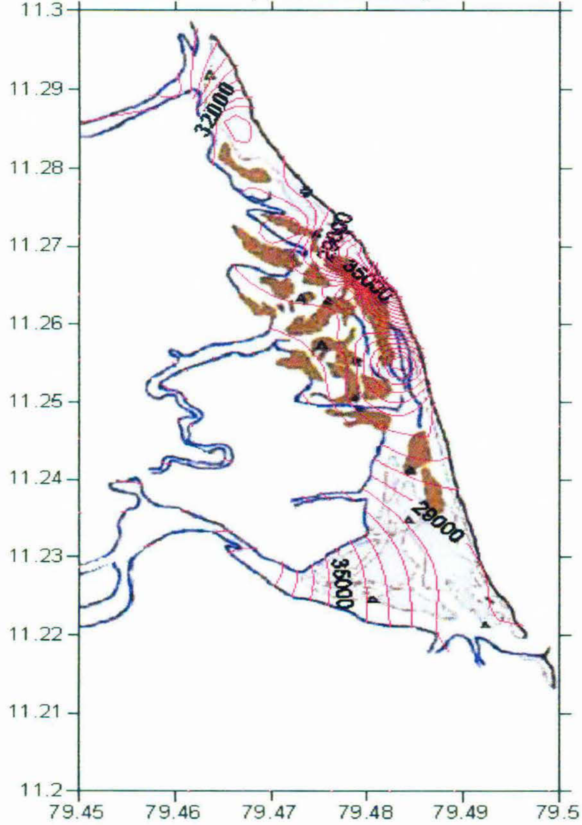


Fig. 4.25 Contour map of Fe (Pre-Tsunami)

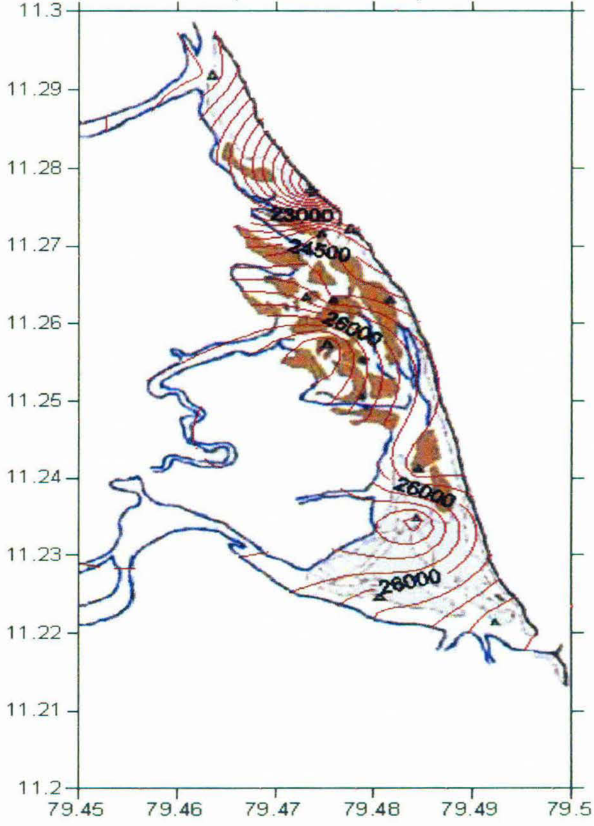


Fig. 4.25A Contour map of Fe (Post-Tsunami)

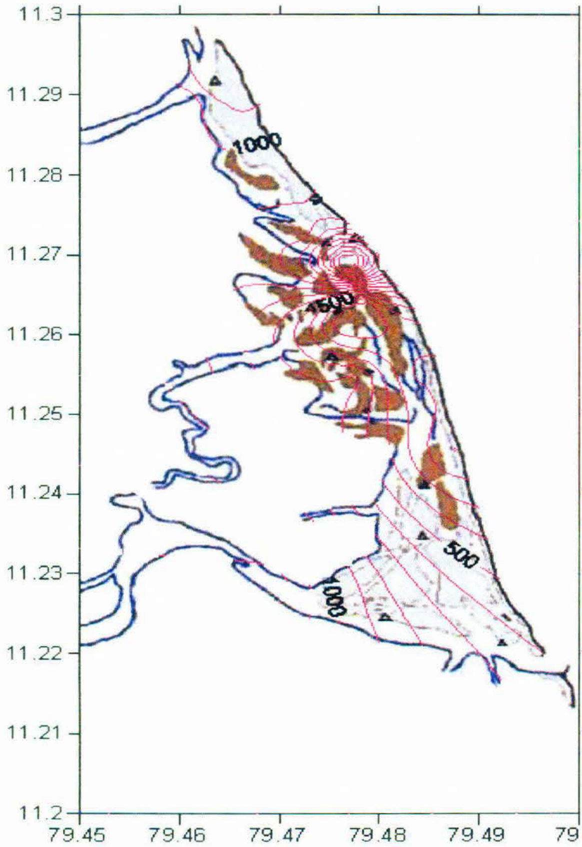


Fig 4.26 Contour map of Mn (Pre-Tsunami)

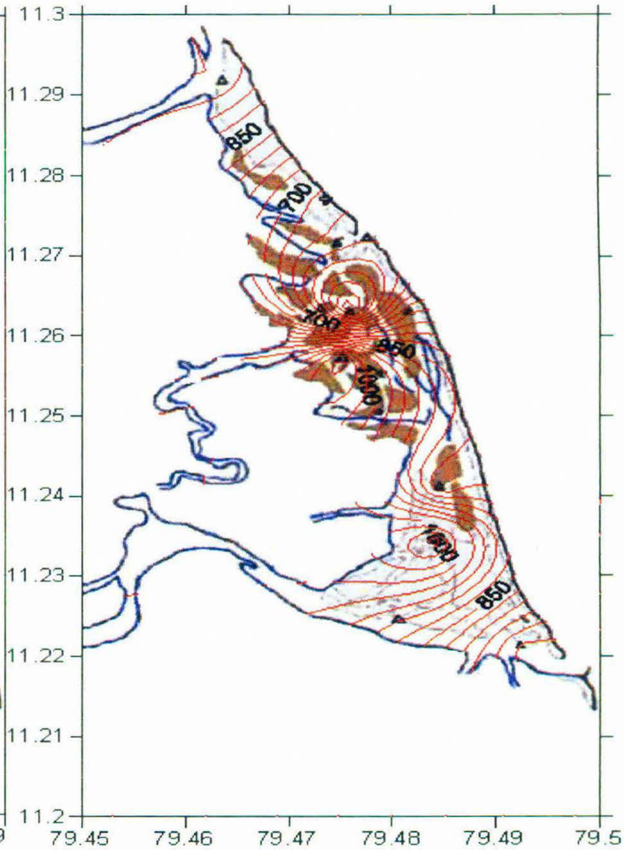


Fig. 4.26A Contour map of Mn (Post-Tsunami)

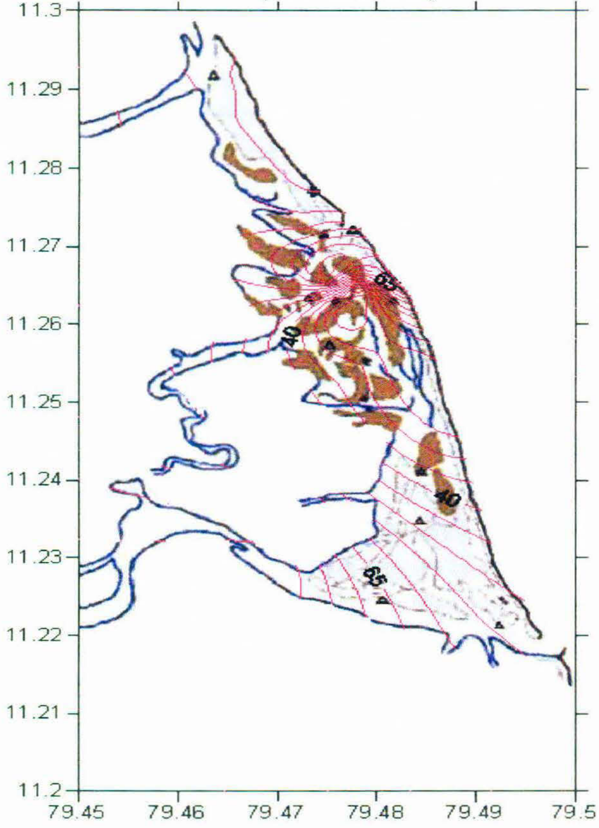


Fig. 4.27 Contour map of Ni (Pre-Tsunami)

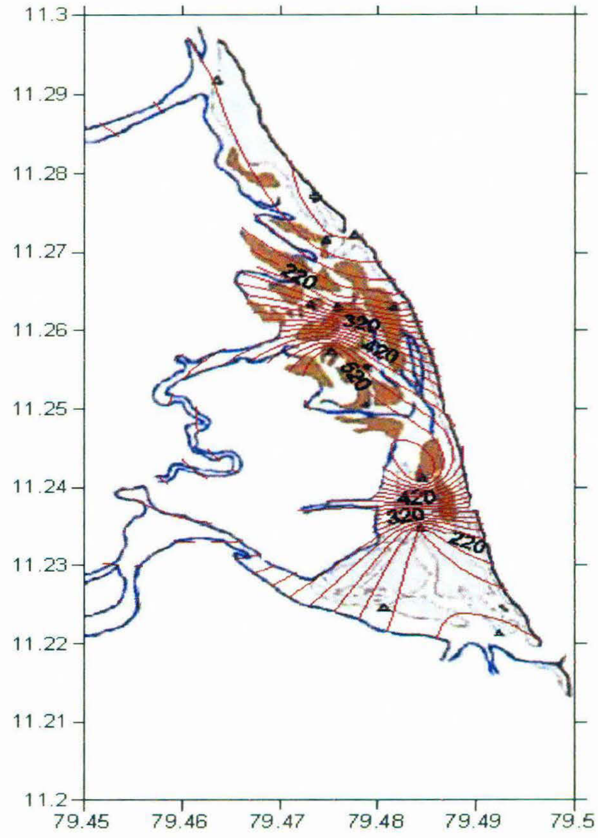


Fig. 4.27A Contour map of Ni (Post-Tsunami)

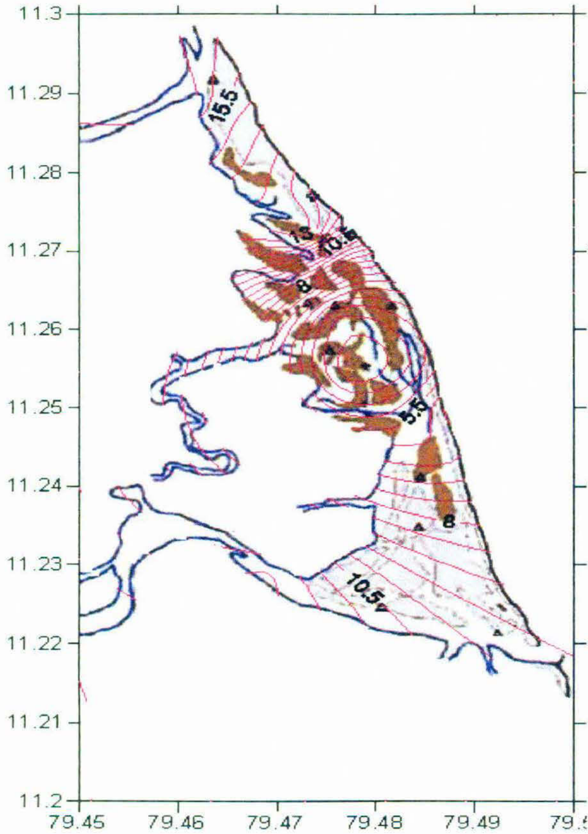


Fig 4.28 Contour map of Pb (Pre-Tsunami)

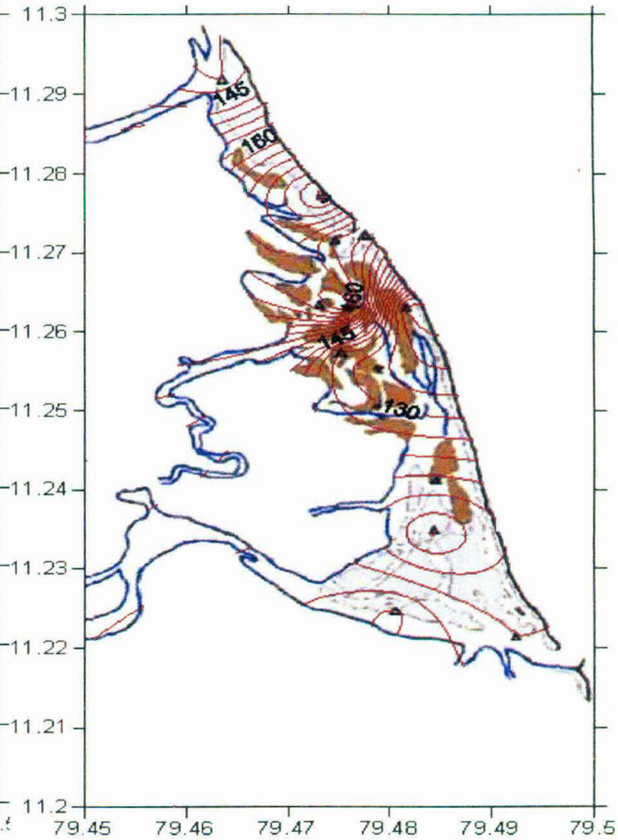


Fig. 4.28A Contour map of Pb (Post-Tsunami)

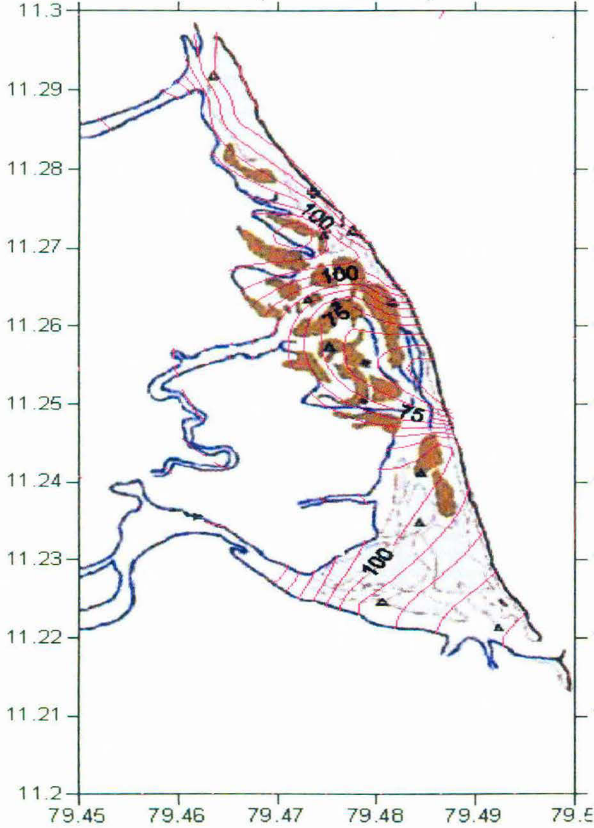


Fig. 4.29 Contour map of Zn (Pre-Tsunami)

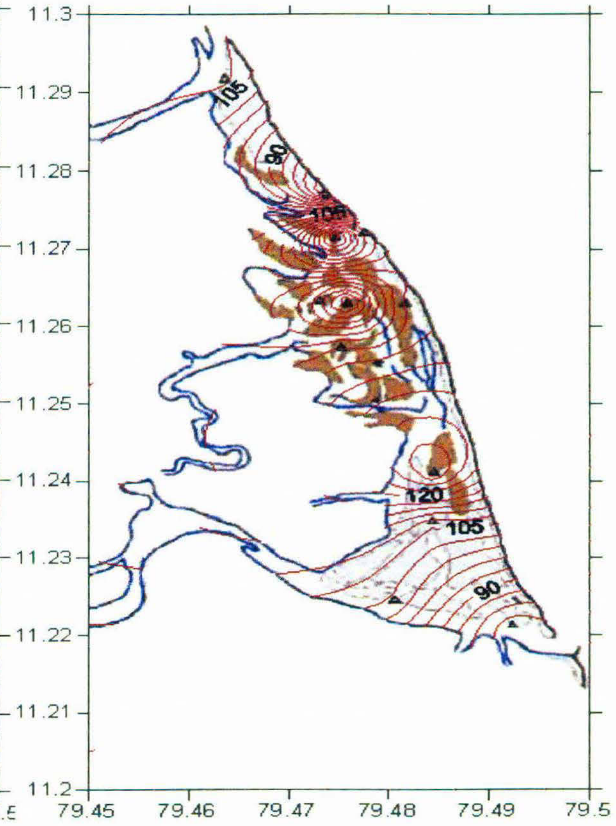


Fig. 4.29 A Contour map of Zn (Post-Tsunami)

Mn, Cu, Ni and Pb show similar behaviour as that of Cd and Cr. However in case of Pb, the contour map shows concentration patches near Vellar estuary indicating that it may have come from pollution caused by diesel. There is a little variation in case of Zn and Fe, which reveals absence of any lithogenic or anthropogenic source as well as shows the conservative nature of these metals.

4.6.3 Correlation between various heavy metals

Fe showed a good correlation with Mn, Ni and Organic matter, where as Fe is negatively correlated with Pb (table 4.12). In the mangrove zone, significant concentration of organic carbon was observed as discussed earlier, this implies that oxic to sub-oxic and then to anoxic vertical gradient might have established in the mangrove sedimentary environment. Organic matter rich sediment have direct control over the redox potential of the sediment and is prime controlling concentration of Fe and Mn in the intertidal sediments (Marchand et al., 2006). Due to changes in redox potential (from anoxic to oxic), desorption of metals (Fe and Mn) from the crystalline sedimentary matrix to the water (Marchand et al., 2006). Thus, higher concentration of Fe and Mn was observed in the water column. Fe-Mn complexes seem to have a strong bearing on the dispersal patterns of other metals in this aquatic sedimentary environment mainly due to their geochemical affinity (Forstner and Wittman, 1983).

Enrichment of Pb, Cd, Co, and Ni in the Pichavaram sediments suggests the effect of discharge of industrial and agricultural wastes through Vellar, Uppanar, and Coleroon River and Khan Saheb canal. The concentration of trace metals in the present study area is relatively high when compared to the reported values (Ramanathan, 1997) of heavy metals concentrations in the sediments of this area. However, the range and average of the metal concentrations of the sediments in the present study are comparable with the measured concentrations of trace metals in mangrove sediments from Brisbane River, Australia (Mackey and Hodgkinson, 1995). Significant correlations of organic carbon with most of the metals (except Ni and Cd) indicate the sediment organic matter is acting as metal carrier and, also their complexation with organic matter playing an important role in their distribution pattern (Samuel and Phillips, 1988). Individual correlations reveal that Cr and Cu have significant correlations with Fe, while, Cr have significant correlations with Mn indicating the probable adsorption of these metals on to the

Table 4.12 The correlation matrix of total Heavy metal in sediments of Pichavaram

Post Tsunami (n=12)

	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	OC
Cd	1								
Cr	0.555	1							
Cu	-0.219	-0.002	1						
Fe	0.459	0.432	0.279	1					
Mn	-0.57	-0.252	0.268	0.524	1				
Ni	0.522	0.669	-0.185	0.526	-0.217	1			
Pb	0.015	-0.47	-0.327	-0.792	-0.337	-0.413	1		
Zn	0.476	0.241	-0.121	0.412	-0.26	0.196	-0.135	1	
OC	0.194	-0.262	0.524	0.569	0.007	0.015	-0.258	0.28	1

oxy-hydroxides of Fe and Mn. Non-significant correlations of Cd, Ni , Zn and Pb with most of the metals may be possibly due to the different processes like biological effects and external inputs operating in mangrove and adjacent estuarine sediments. Ni and Cd having significant correlations with Cr reveal that these metals are carried by industrial waste discharges into the nearby environment. High concentrations of these trace metals in mangrove sediments indicate that the mangrove systems are physical traps for fine material and their transported load of metals constitutes of chemical trap for precipitation of metals from solution (Harbison, 1986).

When the correlation between the heavy metals and organic carbon was studied, it was observed that organic carbon content showed a significant positive correlation with Fe at confidence level of 95%.

The statistical analysis of intermetallic relationship revealed that the high degree of correlation and significant relation among the metals indicate the identical behaviour of metals during its transport in the mangrove environment. There are significant inter-elemental correlations (e.g., Fe-Mn, Fe-Cu, Fe-Cr, Fe-Zn, Cr-Cu, Cr-Ni, Cr-Mn, Cu-Ni,) and inverse correlations (Cd-Cr, Cd-Pb, Fe-Pb, and Mn –Pb) were observed in the mangrove sediments. In the present study, the poor association of Mn with other metals (Ni, Zn, Cu) suggests that Mn-oxide may be only a minor host phase for these elements in the mangrove environment.

4.6.4 Geoaccumulation Index

Mangrove ecosystems, developing in the intertidal zone of most tropical and subtropical regions, are characterized by major contrasts in redox conditions and high rates of organic carbon accumulations (Huc, 1980). They may act as a sink or a source of heavy metals in coastal environments (table 4.14) because of their variable physical and chemical properties (Harbison, 1986).

In order to understand the level of contamination with respect to trace metals, the values of trace metals were utilized to find geoaccumulation index(I_{geo}) While computing the (I_{geo}) of sediments of the study region, world average concentrations of these elements reported for Shale (Turkian and Wedephol, 1961) were taken as the background values.

Increase of heavy metals in the mangrove sediment is primarily due to the enhanced organic matter content, abundance of fine particle with greater surface area (Forstner and Wittman, 1983; Salmons and Forstner, 1984) precipitation of metals as hydroxide coating (mainly Fe and Mn) over finely dispersed particles (Degroot and Allersma, 1975), flocculation due to varying salinity regimes (Sholkovitz, 1976), transportation of deepshore sediments to the coastal zone etc. (Rubio et al., 2000; Seralathan et al.,2006; Ramesh et al., 2006).

Possible sediment enrichment of metals was evaluated in terms of the I_{geo} of Muller (1979). The formula used for the calculation of

$$I_{geo} = \log_2 (Cn/1.5Bn),$$

where Cn is the measured content of element

"n", and Bn the element's content in "average shale" (Turekian and Wedepohl, 1961). The geoaccumulation index (I_{geo}) was originally defined by Muller (1979) for a quantitative measure of the metal pollution in aquatic sediments (Ridgway and Shimmield, 2002) and was applied for the Pichavaram mangrove sediments shown in **Table ..** Elevated I_{geo} values identified for the concentration of Fe, Mn and Zn concentrations observed in present study were quite in accordance with the concentration reported in sediments of various Indian mangrove forests. (Badarudeen et al., 1996; Ramanathan et al., 1999; Ray et al., 2006).

The geoaccumulation index (I_{geo}) values for tsunamigenic sediments indicate that the sediments are extremely contaminated with Cd. The heavy metals like Pb and Cr showed moderately to strongly contaminated nature. Pichavaram estuarine sediment were moderately contaminated with Cu and Ni. The tsunami event had not altered the concentration of Fe and Mn (however only the sampling site 7B.

Table 4.13 Index of Geoaccumulation in tsunamigenic Pichavaram sediments

Index of Geoaccumulation														
Description of sediment quality			Polluters											
	I_{geo}	I_{geo} Class	1	1A	2	4	6	7	7A	7B	8	9	10	11
Extremely Contaminated	>5	6	Cd	Cd	Cd	Cd	Cd	Cd	Cd		Cd	Cd	Cd	Cd
Strongly to extremely strongly contaminated	4-5	5	-	-	-	-	-	-		Cd	-	-	-	-
Strongly contaminated	3-4	4	-	-	-	-	-	-			-	-	-	-
Moderately to strongly contaminated	2-3	3	Cr, Pb	Pb	Cr, Pb	Cr, Pb	Pb	Cr, Ni, Pb	Cr	Pb	Cr, Ni, Pb	Cr, Pb	Pb	Cr, Pb
Moderately contaminated	1-2	2		Cr		Cu, Ni, Pb	Cr, Ni	Cu	Cu Pb	Cr	Cu	Cu	Cr	
Uncontaminated to moderately contaminated	0-1	1	Cu, Ni	Cu, Ni	Cu, Ni		Cu		Mn Ni	Mn		Ni	Cu Ni	Cu, Ni
Uncontaminated	<0	0	Fe, Mn, Zn	Fe, Mn, Zn	Fe, Mn, Zn	Fe, Mn, Zn	Fe, Mn, Zn	Fe, Mn, Zn	Fe Zn	Fe Ni Zn	Fe, Mn, Zn	Fe, Mn, Zn	Fe, Mn, Zn	Fe, Mn, Zn

Table 4.14. Comparison of documented metal concentration in mangrove sediments (Concentration in µg/g)

Location	Mn	Zn	Cu	Pb	Ni	Cr	Fe	Cd
			Sediment					
Pichavaram (Post Tsunami present study)								
	801	**106**	**132**	**146**	**252**	**617**	**24998**	**34.74**
Pichavram[A]								
	941	**93**	**43.4**	**11.2**	**62**	**141.2**	**32482**	**6.6**
Godavari[B]	1059	_	47.8	55.8	25.7	2.20	4575	10.9
Kumarakam [C]	452	236	48	–	–	–	–	–
Panama[D]								
Punta Mala Bay[D]	295	105	56.3	78.2	27.3	23.3	9827	<10
Toro Point[D]	294	19.9	4.9	38	82.4	13.7	1885	6.6
Galeta[D]	143	10.9	4.0	32.5	74	12.8	1748	7.2
Payardi[D]	228	16.1	4.0	33.3	91.8	10	2094	7.5
Costa Rica[D]								
Punta Portete[D]	268	14.7	8.4	34.5	102	22.6	3225	7.3
Punta Piuta[D]	525	11.4	9.8	25.6	99.0	19.8	6118	6.0
Colombia[D]								
Cienaga Grande[D]	623	91.0	23.3	12.6	32.5	13.2	15593	1.92
Australia[D]								
Port Jackson[D]	–	145	62.0	180	–	–	–	–
Port Jackson[cD]	–	351	102	443	–	–	–	–
Hawksbury[D]	–	94	18.9	26.4	–	–	–	–
Port Hacking[D]	–	10.3	1.1	2.5	–	–	–	–
Queensland[D]	103	23–56	1–12	36	9.0	1–72	1056	0.6
Brazil								
Clean Mangrove[D]	–	24.2	3.82	–	–	–	2464	0.6
Hong Kong								
Clean mangrove [D]	-	96	43	2.6	31.2	2.9	1.2	1.08
Asia								
UAE[D]	28.64	7.78	1.83	11.78	2.34	6.68	1593	1.06
Arabian Gulf [D]	28.8-169	4.59-22.4	5.31-2.94	13.2-49.8	14.8-109	8.28 18.9	-	3.12-6.94
Goa[D]	767	-	26	-	52	-	-	-
Futian China[D]	-	7.26	-	14.97	2.52	-	-	0.72

A Ramanathan et al, 1999
B Ray et al 2006,
C Badarudeen et al, 1996,
D Singh et al, 2005

As Tsunami leave behind a clearly identifiable sediment deposit (Dawson and Shi 2000; Schaffer and Kelletat, 2003) and is buried and preserved, then in due course of time, a geologic record of that tsunami will be created. However, the interpretation of their origin requires study of many diagnostic sediment properties—for example: grain-size Fining trends, character of lower and upper contacts, presence of intraclasts, marine diatoms, foraminifera and other microfossils, etc (Goff et al., 2001). Sediment chemical composition was also used as a proxy helping identification of paleotsunami sediments. The residence time of post-tsunami seawaters in the sediments and, in consequence, the amount of bounded contaminants may be partly related to grain-size distribution (Szczucinski et al., 2005).

The exception is Pb, which in seawater belongs to the least common heavy metals (Riley and Chester, 1983) and in the studied sediments; its concentrations are the highest (Table 4.13). It would indicate distinct source of this element—lithogenic or anthropogenic.

4.6.5 Speciation of metals in Tsunamigenic sediments

The biogeochemical behavior of the heavy metals and their chemical forms can be studied with the help of fractionation (Prasad et al., 2006). The metals present in, water soluble, exchangeable and carbonate fractions are considered to be weakly bound and have equilibrium with the aqueous phase and hence are readily available to the biological systems. Some amounts of heavy metals are strongly bound to Fe -Mn oxides and organic matter which act as internal reservoirs. On the other hand, the metals in the residual fraction are not available under normal conditions. The hydrous Mn-oxide fraction exhibits more isotropic substitution than amorphous Fe-oxide and shows greater conditional equilibrium constants for heavy metals than crystalline Fe-oxide (Kotoky et al., 2004). From the pollution point of view, the total metal content of the sediments is of less importance than that fraction of the metals which resides outside the crystal lattice, or can easily mobilized (Waldichuk, 1985). According to different studies, (Chester and Hughes, 1967; Chester and Hanna, 1970; and Agemain and Chau, 1976), metals in sediments may be classified as lattice-held (residual), and non-lattice held (non-residual). Source materials primarily control the heavy metal concentrations in residual fraction. This feature reflects the predominance of

Figure 4.30 Speciation of Cd in Tsunamigenic Pichavaram Sediments

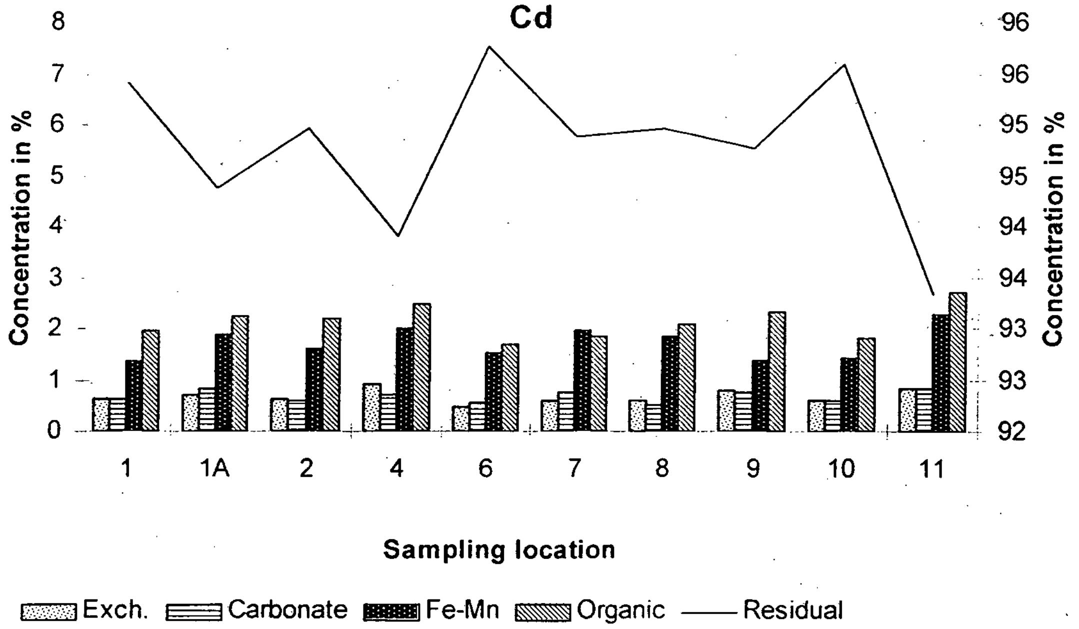


Figure 4.31 Speciation of Cr in Tsunamigenic Pichavaram Sediments

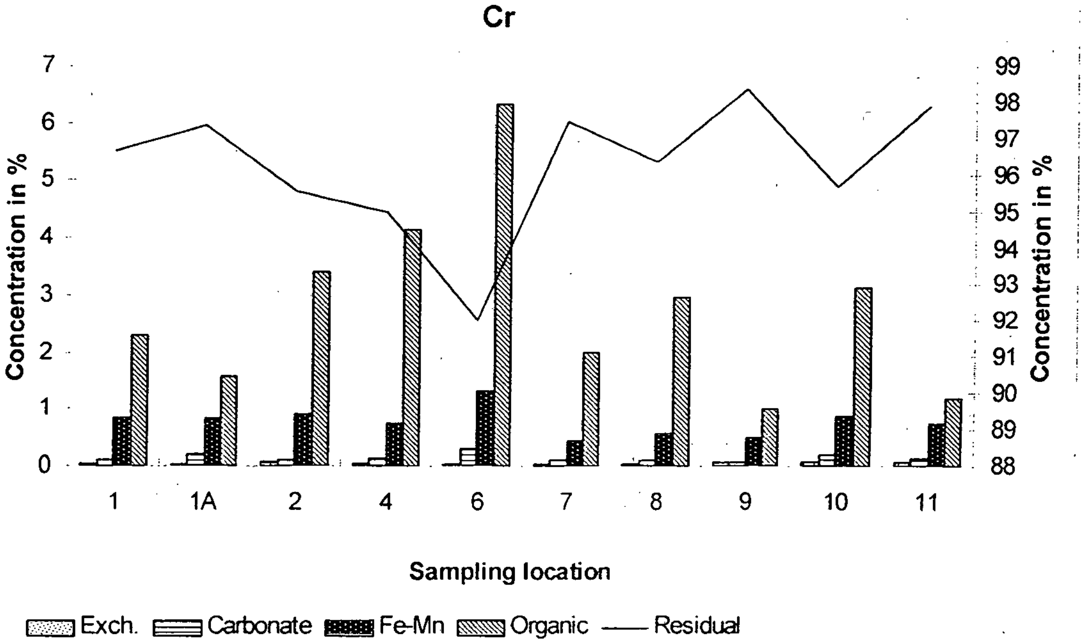


Figure 4.32 Speciation of Cu in Tsunamigenic Pichavaram Sediments

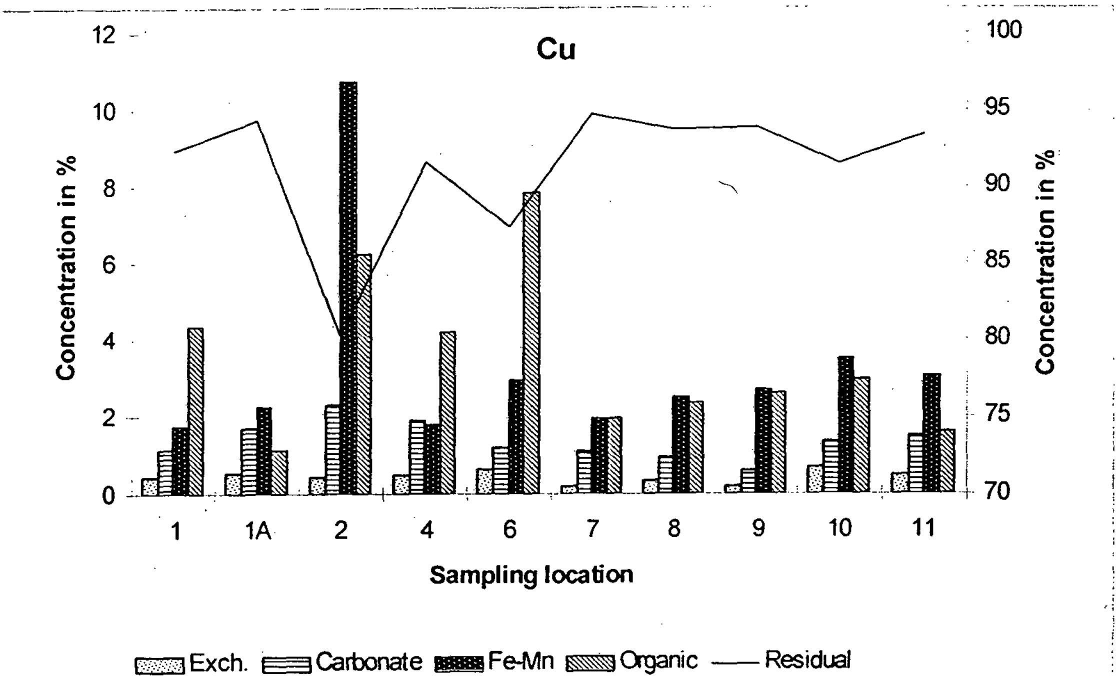


Figure 4.33 Speciation of Fe in Tsunamigenic Pichavaram Sediments

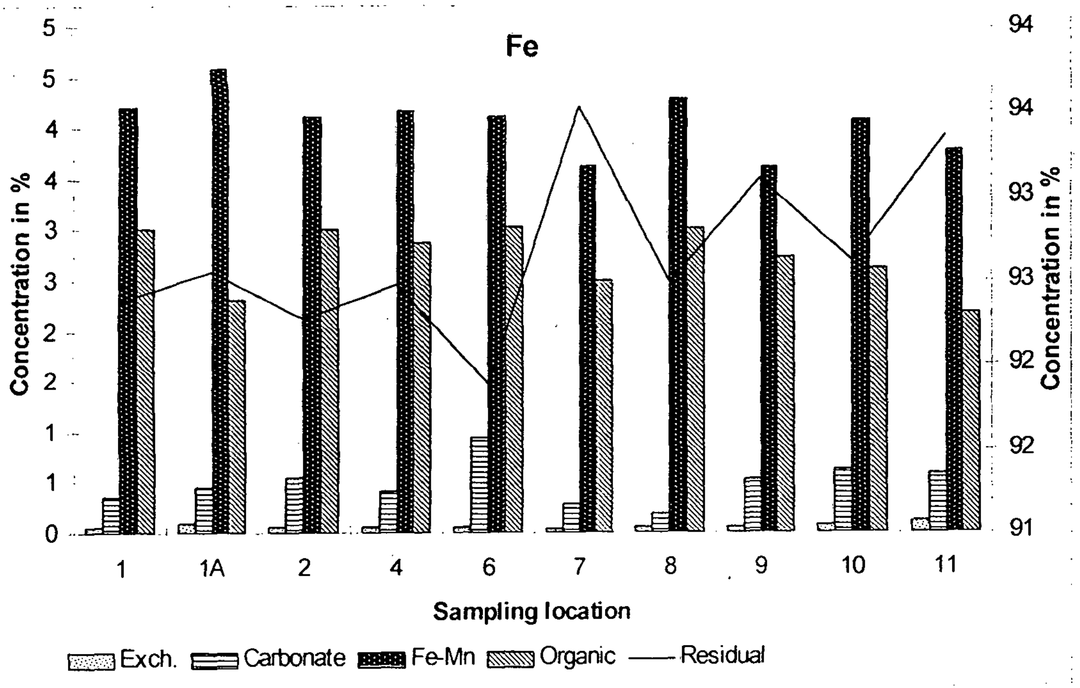


Figure 4.34 Mn Speciation of Mn in Tsunamigenic Pichavaram Sediments

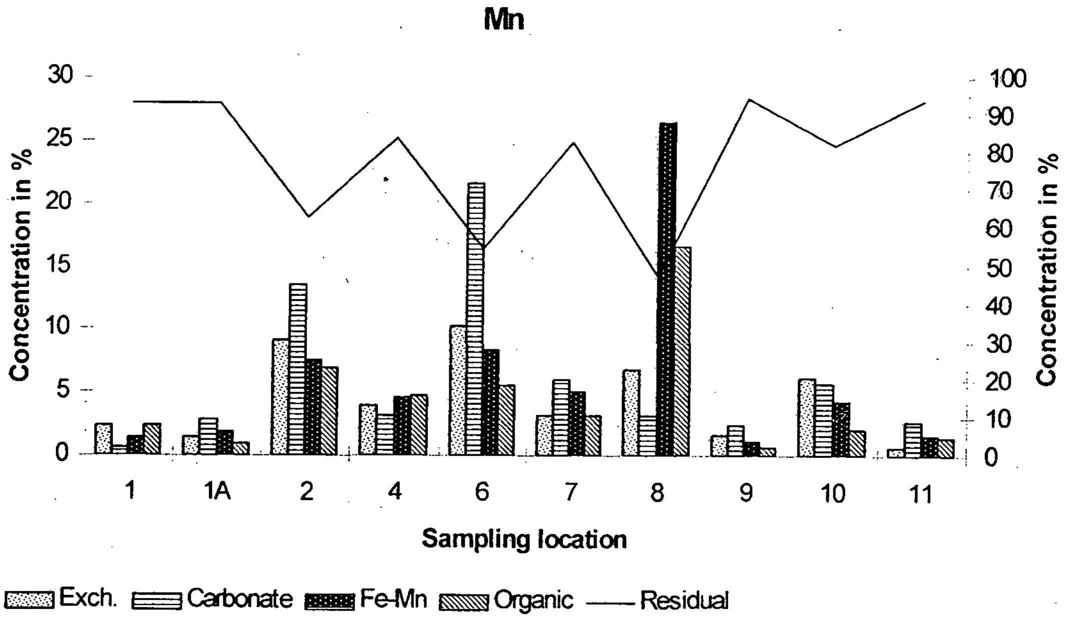


Figure 4.35 Speciation of Ni in Tsunamigenic Pichavaram Sediments

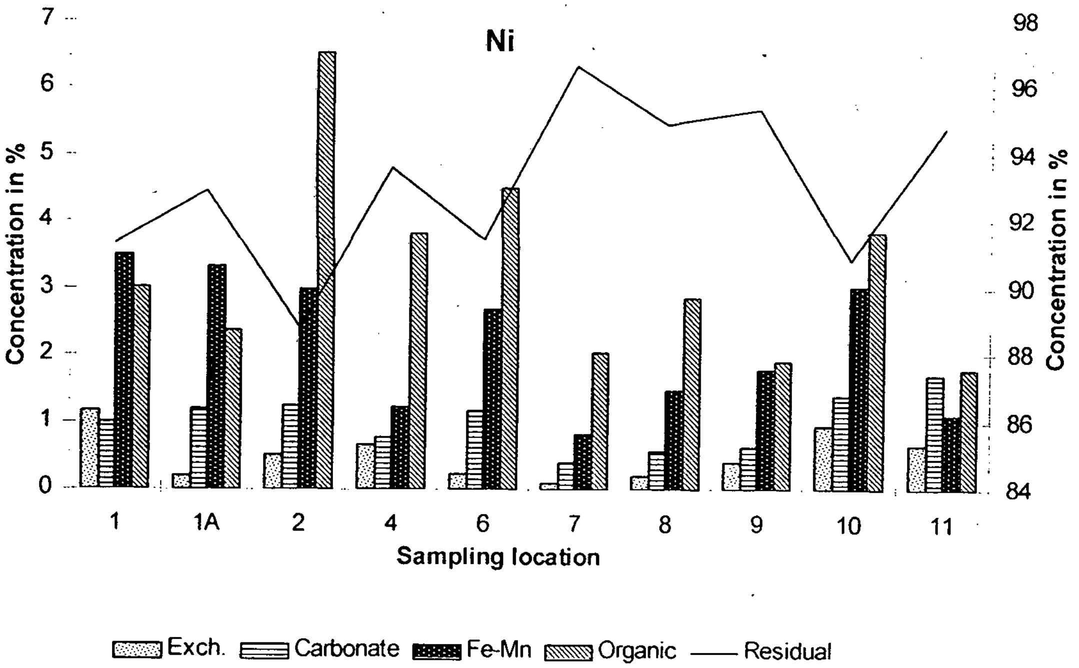


Figure 4.36 Speciation of Pb in Tsunamigenic Pichavaram Sediments

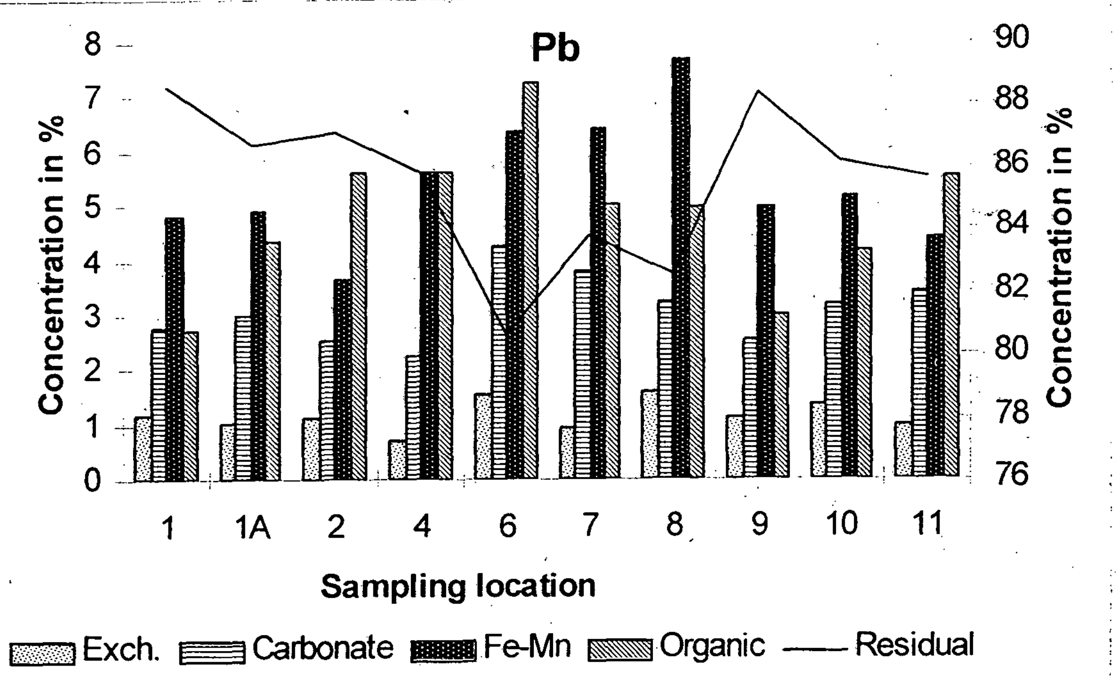
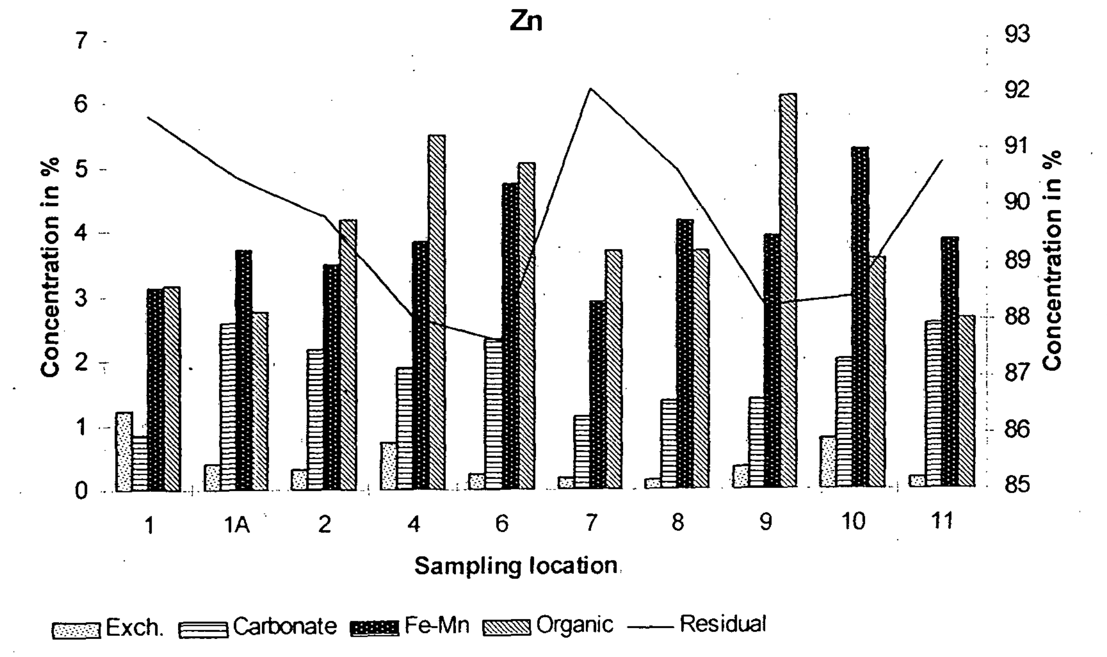


Figure 4.37 Speciation of Zn in Tsunamigenic Pichavaram Sediments



Physical weathering and high erosion rates in the drainage basin. The metals present in the residual fraction can be used as a baseline data for the assessment of the degree of the contamination of the system. Greater percentage of metals present in the residual category indicates lower pollution, because this inert phase corresponds to detrital or lattice bound metals that cannot be remobilized. The cycling of heavy metals, because of their toxicity, bio-accumulation capacity and persistence, is a serious question recently addressed by many studies on mangrove environments (Harbison,1986; Lacerda et al., 1988; Mackey and Hodgkinson, 1995; Tam and Wong, 1995, 1997, 2000; Clark et al., 1998). The metal speciation of heavy metal in the present study revealed that most of the metal species were found in residual fraction.(Fig.. 4.38-4.45) and least in exchangeable fraction. Organic bound metal are also playing a major role in the biogeochemical cycling of the metal in this area. The high concentration of organic carbon (10180 μg /g) and high Organic Carbon/ Nitrogen ratio (16.374) showed that there was huge amount of organic matter in study area, that's why the organic bound metal was present in a large amount.

The chemical partitioning trend was found to be different for each metal. However in all metals, 80-90% of metal species was dominated by residual fraction. The similar result was also observed in the lower estuary of Cauvery River, (Ramanathan et al., 1993). The concentrations of various fractions of metal species are given in μg /g determined at each extraction step in the sediment samples.

Like other metals, last fraction (residual phase) was most dominated one in the entire fraction followed by organic>Fe-Mn>Carbonate=Exchangeable. The high values of Cd in organic bound fraction indicated that Cd occurred in the form of stable organic complexes and metal sulphides. Under an oxic water column a significant amount of the metal reaching the sediment interface may be returned to the overlying water column by mineralization of the host organic matter at the surface, and in the oxic upper layers of the sediment (Petersen et al., 1995). The preferential association of Cd, Pb, and Mn with the carbonate fraction can be attributed to the high stability of their respective carbonate complexes under pH-Eh conditions of the Pichavaram mangrove sediments as well as to their co precipitation with calcium carbonate (Salmons and Forstner, 1984, Ramanathan et al., 1993). Significant amounts of Cd were also found in exchangeable fraction compared to other heavy metal sinks due to their mobility and possible derivation from human influences (Forstner, 1983).

Although the mean concentration of Chromium has increased by 4.5 times than the previous study (Ramanathan et al., 1999) but rest all fraction were very less in compare with residual fraction (96.23 %) the rest lees than 4% metal of Cr was followed like Organic bound > Fe-Mn bound >Carbonate>Exchangeable. The Cr concentration up to 5% had been reported to be bound in the humic acid fraction of the soil (Bodek et al., 1988). The high amount of Cr in the organic fraction may be due to the scavenging effect. Singh and Subramanian (1984) explained that Mn-Fe oxides act as efficient scavengers for many of the heavy metals (Fe, Mn, Cu, Cd, Cr, Ni, Zn). Relatively higher concentration of Cr associated with this fraction was caused by the adsorption of Cr by the colloids of Mn and Fe (Jenne, 1968). Cr was well correlated with Fe, and Mn, so fate of Cr was also dependent on Fe-Mn oxide in that sedimentary system.

Copper showed the trend as Residual>Organic bound>Fe-Mn bound>Carbonate bound>Exchangeable when the different fraction were considered. Copper is preferentially retained on the organic matter by complexation rather than by ion exchange (Balasoiu, 2001; Wu et al., 1999). This strong effect can also be attributed to the fact that copper easily forms complexes with the organic matter due to high stability constant of organic Cu compounds (Kotoky, 2004). Organic matter exhibits a high degree of selectivity for divalent ions and hence the organic bound Cu fraction is an important fraction in the sediments and is not available to the biological activity (Mcbride, 1994).A significant amount of Cu is associated with the Fe- Mn oxide form by co-precipitation or by sorption onto preexisting coatings under existing physicochemical conditions (Panda et al., 1995). During early diagenesis, microbially mediated redox reactions quickly result in the reduction of some of the insoluble Fe (III) and Mn (II) oxides, and the release of Fe (II) and Mn(II) species to the pore water (Canfield, 1989). Also a good correlation between Cu and Fe showed that the Cu and Fe are associated to each other. A significant amount of Cu is associated with carbonate bound and as an exchangeable fraction. $CaCO_3$ in the carbonate phase is not a significant contributing factor to the heavy metal content of sediments (Paropkari et al., 1980). Metals bound to these different phases will behave differently in the sedimentary and diagenetic environment, and thus have different potentials for re-mobilization and for uptake by biota. Thus, it is readily available and relatively mobile for biological uptake, a process facilitated by the lowered pH (Copeland and Ayers, 1972).

Occurrence of Fe was in total fraction was as follow Residual>Fe-Mn bound>Organic>Carbonate bound>Exchangeable. Higher fraction of Fe present in the residual from came from the weathering of minerals viz. feldspar etc. via the vellar, Upnnar and Coleroon river. The Fe-Mn oxide bound Fe present phase might be attributed to the flocculation of colloids of Fe in Pichavaram mangrove sediments. The organic matter also contains significant amount of Fe. The good correlation between Fe and organic C (0.6) showed that the Fe associated with organic matter was playing a major role in the biogeochemical cycling of this metal in Pichavaram mangrove sediments. The carbonate and exchangeable fraction of Fe was less in compare to other fraction showed that Fe was less bio available to biota in the sediments.

The Chemical fractionation studies showed that the residual fraction holds high amount of metals in comparison to other fraction, in the case of Mn the fraction followed the trend Residual> Fe-Mn bound> Carbonate bound>organic bound > Exchangeable. It is well established that Fe and Mn oxides exists as nodules, concretions, cement between particles or simply as a coating on particles, these oxides are excellent scavenger for trace metals and are thermodynamically unstable under anoxic conditions i.e., low Eh (Jenne, 1968). Carbonate and organic bound fraction were present in the sediments was also in significant quantity. The Fe associated with carbonate was less than organic bound, whereas in Mn the condition was in reverse order.

The fractionation of Ni showed that the Ni was present in the sediments was as follow-Residual>organic bound>Fe -Mn>Carbonate>exchangeable. The residual fraction was also dominant fraction among all fractions. Ni was well correlated with Cr and Cu, so fate of Ni in this system must be same as these metals up to some extent.

The fractionation of Pb shows that its major fractions are associated with Residual fraction followed by Fe-Mn bound >Organic bound>Carbonate bound>Exchangeable fraction(. A significant quantity of Pb probably originates from weathering of rock rich in manganese oxides and amorphous iron oxides. Hence concentrations of Pb is highest in Fe- Mn oxides bound fraction, possibly due to the formation of a stable complex (Lopez Sanchez et al., 1996; Jones and Turkie, 1997).

Although the exchangeable fraction was quite less than other fraction. The lower concentration of Pb in the exchangeable fraction suggests its low bio-availability. Fairly higher concentration in carbonate fraction indicates a change in the physiochemical parameters of the ecosystem that may also dissolve the carbonate bound fraction in water becoming a potential hazard to the biological production (Prasad and Ramanathan, 2006).

Like other metal Zn was also dominated in residual fraction followed by; Organic bound, Fe-Mn bound, Carbonate bound and Exchangeable. The same trend was also observed with Cd. Zn and Cd being in the same group of the periodic table. In natural system up to many extents, they both show the same reaction kinetics. Zn was well correlated with organic carbon (0.54) in surface sediments. The Zn concentration up to 5% is reported to be bound in the humic acid fraction of the soil Relatively higher concentration of Zn and other heavy metals associated with this fraction are caused by the adsorption of these elements by the colloids of Mn and Fe (Jenne, 1968). The sorption of zinc with iron in the sediment may strongly hinder their mobility in the aquatic environment. A minor amount of Zn is associated with carbonate and exchangeable fractions. Calcium carbonate forms complexes with zinc as a double salt ($CaCO_3 \cdot ZnCO_3$) in the sediment (Li et al., 2000). Low concentration in exchangeable fractions indicates low bio-availability of Zn.

4.6.7 Speciation of Heavy metals in core sediments

Mangrove is behaving as a sink for Cd. In all cores, the residual phase is the dominated, which is not available for the biological activities. However in core 2 and 3 , in the middle portion., organic bound fraction is the dominant(Fig. 4.38) .Alongi et al. (2005) reported that significant microbial mineralization was taking place in the sediment of Pichavaram. Therefore, a slight change in sedimentary

Figure 4.38 Speciation of Cd in core sediments

Concentration in μg/g

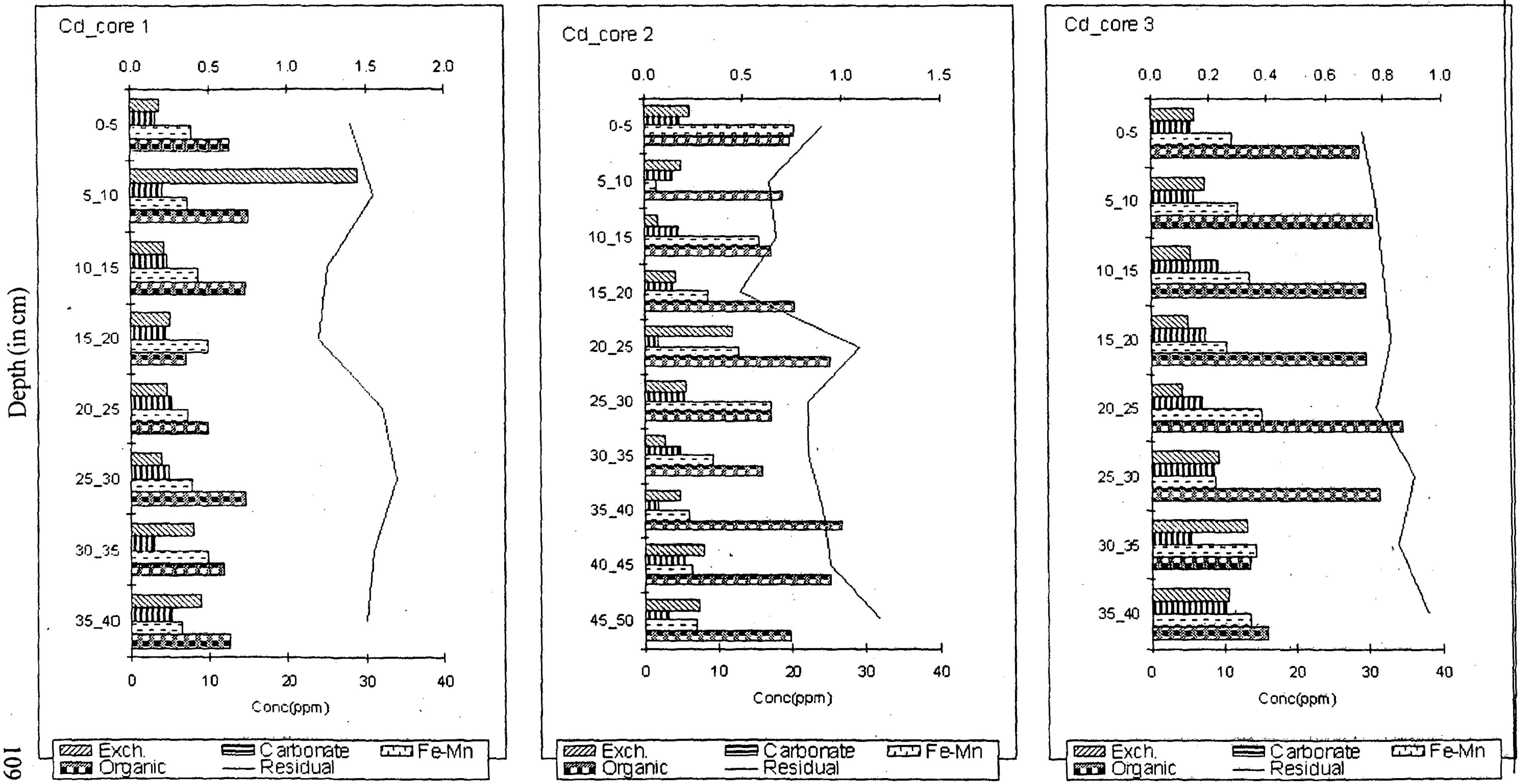


Figure 4.39 Speciation of Cr in core sediments

Concentration in μg/g

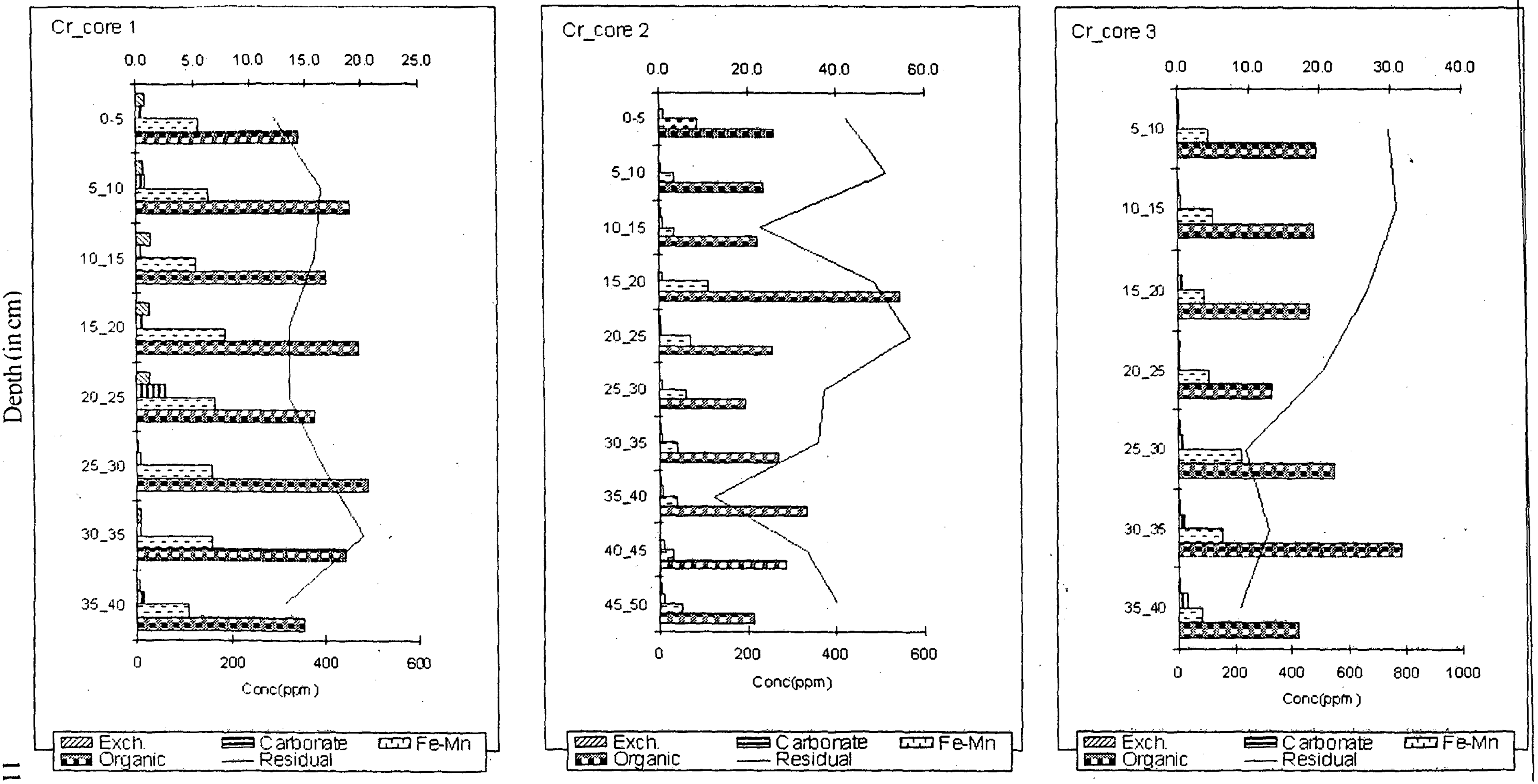


Figure 4.40 Speciation of Cu in core sediments

Concentration in µg/g

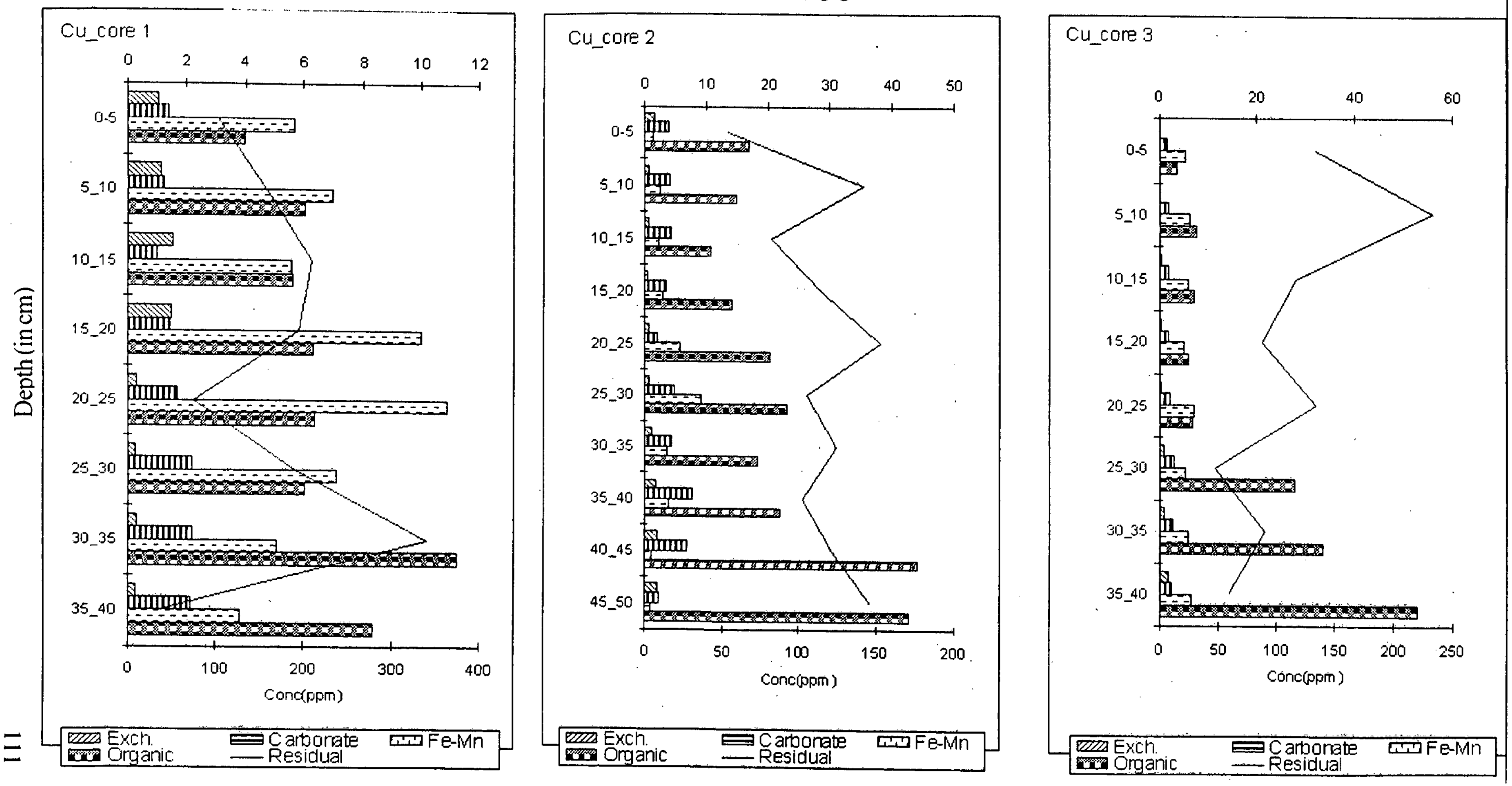


Figure 4.41 Speciation of Fe in core sediments

Concentration in µg/g

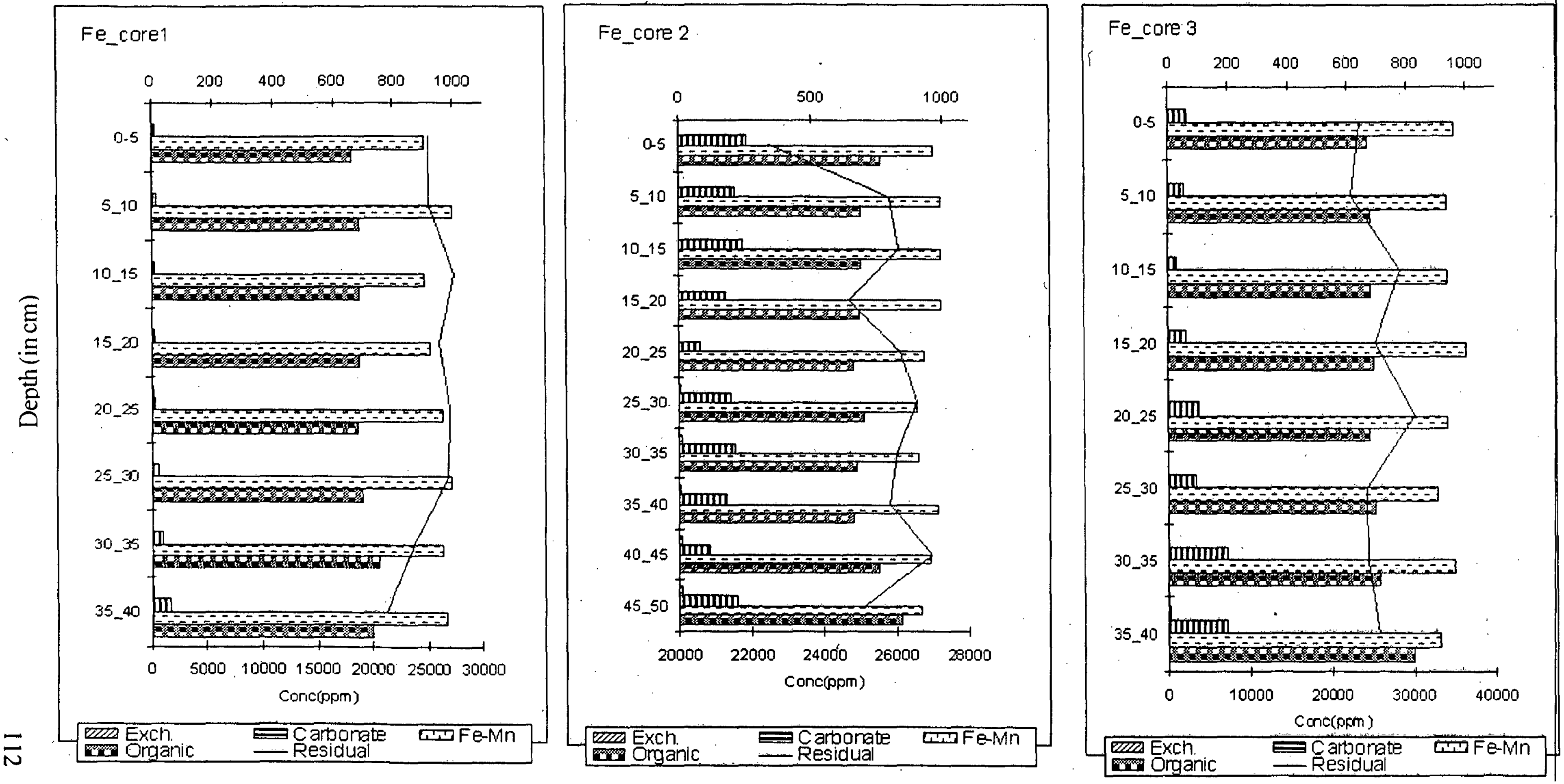


Figure 4.42 Speciation of Mn in core sediments
Concentration in µg/g

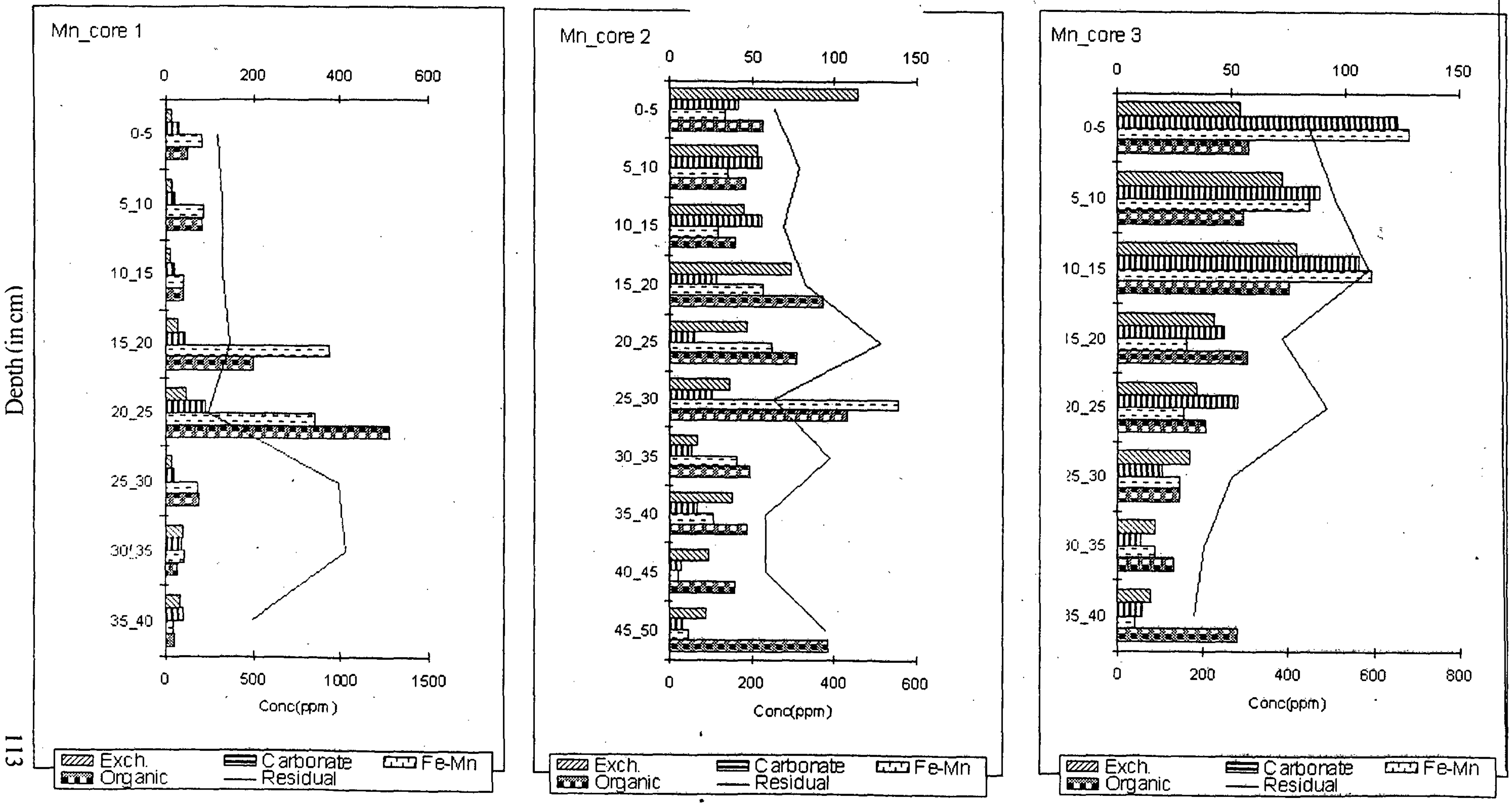


Figure 4..43 Speciation of Ni in core sediments
Concentration in μg/g

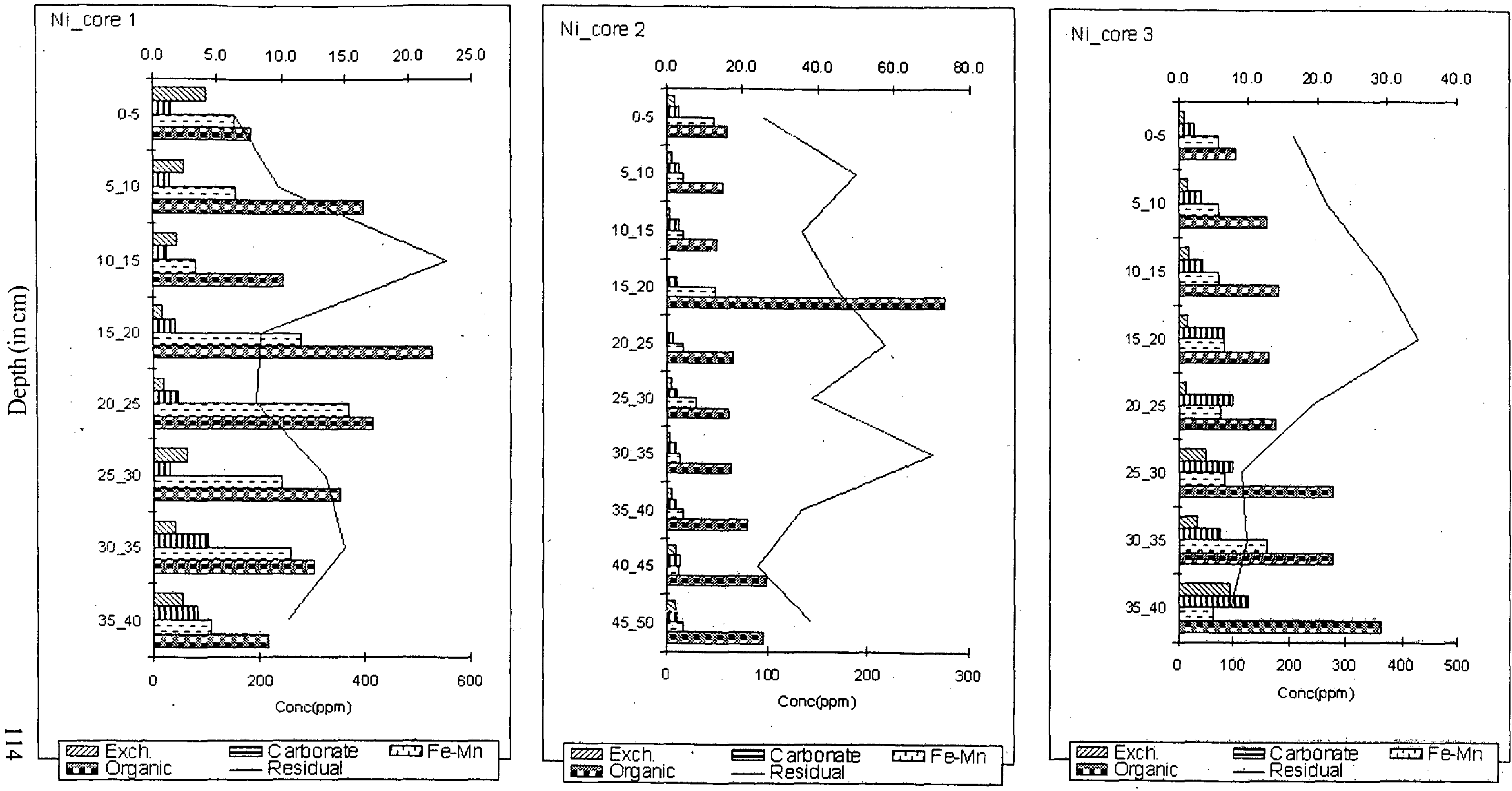


Figure 4.44 Speciation of Pb in core sediments

Concentration in µg/g

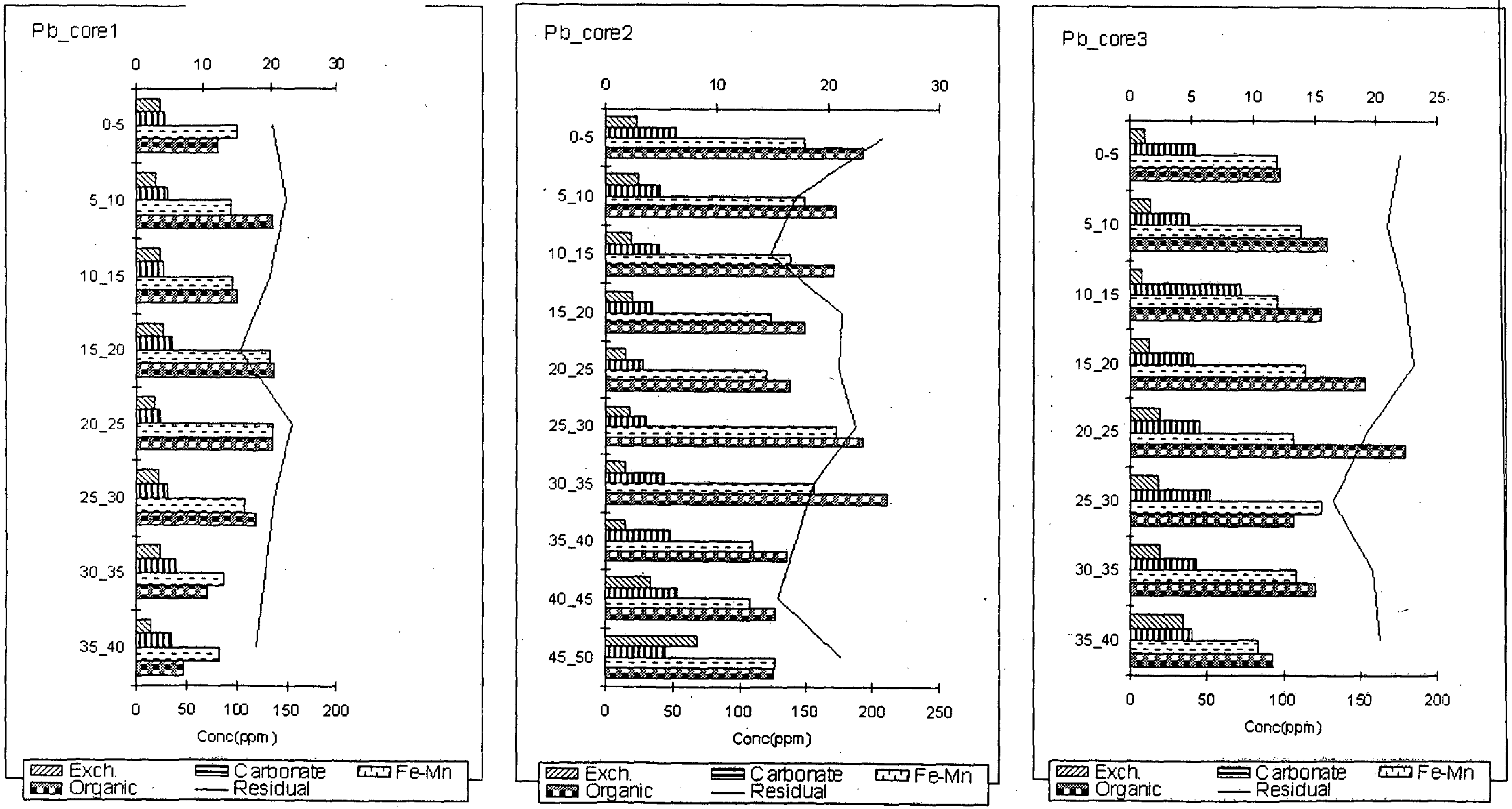
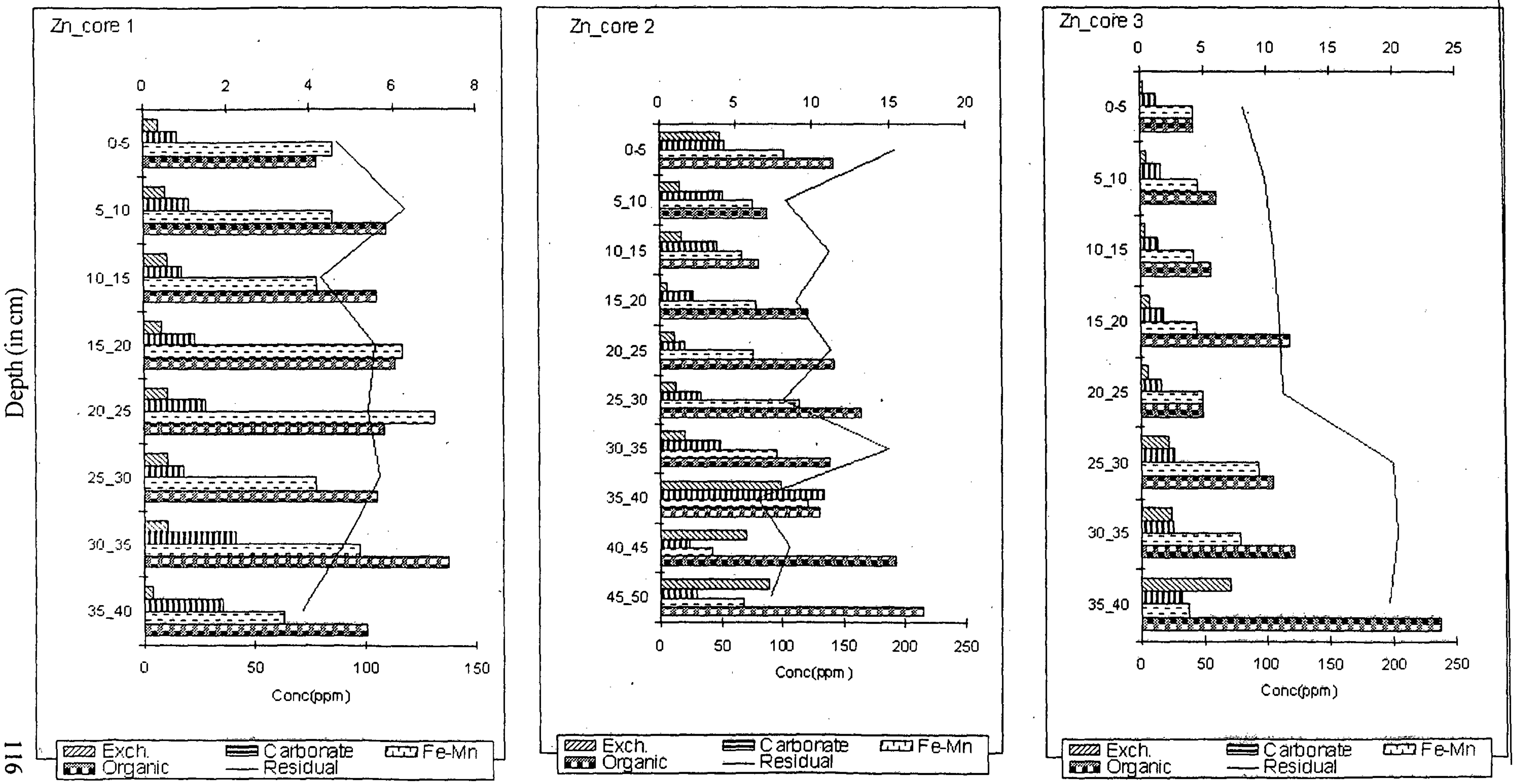


Figure 4.45 Speciation of Zn in core sediments

Concentration in µg/g



environment along with microbial activity leads to release of Cd from organic molecules and dissolve in pore water, which eventually enhances the Cd concentration in the surface water by means of bioturbation and diagenetic processes.

Major fraction that dominated the Chromium chemistry in the Pichavaram estuarine complexes was the organic fraction and residual, which indicated that Cr is mainly derived from adjacent terrestrial system. Khan et al., (2004) has described the presence of 43 industrial units (mainly chemical and pharmaceutical units, set by SIPCOT) discharging their waste through Uppnar river to the mangroves .As a results persistant pollutant are deposited on the sedimentary bed with time. Apart from that, presence of fishing habour at Vellar and aquaculture waste discharge thas contributed to the increase in the organically bound Cr in the sediments. In core 1, since it is from the Vellar zone, Fe-Mn and organic bound phase are the dominant. This indicates the external deposition is the main source. Whereas in core 2 and core 3, up to 20-30cm, less concentration of all fraction has been observed and deeper parts organic bound fraction is the major fraction. This indicates that, surface concentrations were washed out by the tsunami waves.

Like Cu, in core 1, the considerable level of various fraction of Ni has been observed. But in core 2 and 3, low levels of various Ni fractions is noticed, this is due to washing effect. However in the middle layers, higher levels of organic bound fraction are dominant, this is due to post depositional changes.

Fe showed more or less conservative behaviour with depth. High organic bound Fe can be attributed to the complex nature of mangrove estuarine environment. In case of Mn no regular trend was observed, exepct for the core-3 where a decrease in the all fraction was notice with depth Higher levels of Pb in organic and Fe-Mn bound fractions have been observed. This may be mainly derived from the anthropogenic sources. Since oxide bound is dominant along with organic, if there is any changes in the sedimentary environment, leads to release of Pb to the surface water, which leads to harmful effects on biological system dynamics. In all cores, Zn is bound to organic fraction followed by Fe-Mn fraction. It indicates that along with Pb or it is derived from terrestrial land masses and deposited in the tsunami sediment.

Chapter 5

Summary & Conclusions

Mangrove forests are highly productive environment after the rain forests. It has been well documented that it provides number of ecological, educational and economic services to the human society. At the same time, it also controls the global biogeochemical cycles of nutrients and supplies considerable amounts of nutrients for the oceanic biological productivity (Dittmar et al., 2006). The mangrove environment is highly vulnerable not only to the natural hazards but also impacted by human disturbances (Alongi et al., 2005). The current project has been designed to assess the impact of recent tsunami in the Indian Ocean on 26 December 2004 on the Pichavaram mangrove of south east coast India. Danielsen et al., (2005) reported that the mangrove vegetation along the south east coast of India acts as a shield to protect the human settlements from the killer tsunami waves. However, the giant tsunami waves have changed the various ecological parameters of the mangrove environment, which certainly have a significant impact over the nutrient cycles. In order to assess the tsunami impact, water and sediment (surfacial and core) were collected and analyzed for nutrients, metals and other parameters. It has been observed that there are significant changes in the nutrients and metals concentrations in the Pichavaram mangroves. The results of this project are summarized as following

- Significant spatial variations in nutrient concentration in mangrove water have been observed; this is mainly because of mixing of different water masses, derived from adjacent terrestrial landmasses and from the deposited sedimentary environment.
- Dissolved oxygen (DO) is the prime controlling factor of primary productivity along with salinity, it has increased from 5.5 mg/l to 8.3 mg/l, and this is mainly due to high turbulence and mixing of different water masses after the tsunami, which facilitates the dissolution of atmospheric O_2 in the mangrove water column.
- Salinity has increased by around 45%; this is mainly because of mixing of neretic water from the Bay of Bengal. After tsunami, the marine water got accumulated within mangrove ecosystem, thereby increasing the salinity. The salinity has significant correlation between various nutrients; it

implies that it has a strong control over the nutrient dynamics in the Pichavaram mangrove waters.

- All nutrients are increased in the tsunami water, but ammonia concentration is highly increased compared to other nutrients, this is mainly derived from the pore water by the bioturbation.
- Mean size of the tsunamigenic sediments ranges from 1.9 Φ to 3.06 Φ (avg. 2.38Φ), this indicates that the sediments are very fine-grained and are deposited by inner shelf processes. In contrary, before tsunami the mangrove sediment was mainly medium-fine grained in texture.
- The average standard deviation of tsunamigenic sediment is 0.97 Φ while before tsunami its value was 0.7 Φ; this indicates that sediment have become moderately well sorted to poorly sorted.
- A significant variation is also found in skewness. Before tsunami its mean value was 0.32 Φ, but after tsunami it had increased to 0.92 Φ. The pre-tsunami sediment was fine skewed and now after tsunami, it is a combination of coarse and fine skewed sediment.
- The pre-tsunami kurtosis value was an average of 0.81, but post tsunami the value has increased to 1.82. Around 50% of the samples were very platykurtic, 10% are platykurtic and 40% were leptokurtic in nature of distribution. The indicated very platykurtic to leptokurtic with a meso-kutic character.
- Finer fractions have strong control over the nutrient distribution in the mangrove sediments, as this, fraction have more nutrients than coarse grained sediment.
- Vertical increase in nutrients has been observed from top to bottom.
- Clear spatial variations in heavy metal concentrations have been noticed. This implies that the tsunami sediments are contaminated by the heavy metals that are due to leachate brought back by inundation during tsunami and from agriculture and aquaculture.
- Higher concentrations of metal are in residual and organic fractions have been observed in core samples. Further, some metals (Cd, Fe and Mn), higher levels are found in Fe-Mn oxide bound fractions. But at the

surface, low levels of metals observed; this is due to wash out effect of tsunami waves. At some places at the middle, considerable levels of Ni in oxide bound fraction is noticed, this is due to post-depositional effect.

- Phosphorus is the limiting nutrient for the biological productivity. In the tsunami sediments, P is found in oxide bound followed by organic and detrital fractions. Before tsunami, there a decrease in adsorbed, oxide-bound P, while increase in authigenic, detrital and organic P. Low levels of P at the top layer are because of absorption of available P on the sedimentary particles. Adsorbed 'P' increases in general after tsunami in the undisturbed zone. Oxide bound 'P' has increased after tsunami.The impact of tsunami is clearly visible in case of 'P' fractionation. The organic P, which is generally generated in mangrove area, has been washed back with ocean or may be available for coastal productivity. The oxide bound P might have derived from the retreat of waves after tsunami from the two estuaries which is abundant here and may not be available to system either due to change in Eh of sediment, it may be available.

Thus it can be concluded that after tsunami, there is a significant alteration in the sediment composition and characterization.

But still, all reasons of changes is not yet rule out, which requires more extensive and long term studies on much more aspects.

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Appendices

Appendix 1. Weight Distribution in different grain size

Particle size in µm

SAMPLE ID	>250	250-125	125-63	63-50	50-30	30-20	20-10	10--5	<5	Total Wt in gm
1	1.72	29.93	42.92	18.3	4.24	0.91	0.58	0.27	0.27	99.14
1A	15.8	75.65	6.5	1.6	0	0	0	0	0	99.55
2	6.31	40.2	45.74	4.38	1.22	0.82	0.97	0.04	0.02	99.7
3	14.34	74.38	10.69	0.48	0	0	0	0	0	99.89
6	18.9	41.4	22.3	13.5	1.79	0.88	0.6	0.33	0.2	99.9
7	21	39.4	20.21	9.16	4.78	2.64	2.13	0.21	0.07	99.6
8	49.3	20.71	12.95	3.05	2.92	2.94	3.52	3.67	0.22	99.28
9	17.65	67.7	10.25	3.43	0.45	0.13	0.03	0.04	0.02	99.7
10	10.18	38.62	30.1	16.27	2.52	1.04	0.64	0.26	0.17	99.8
11	28.32	48.8	17.2	5.5	0	0	0	0	0	99.82

Appendix 2. Values of Nutrients in Post tsunami sediments

SampleID			**Concn.(*10^3µg/g)**							
	Al	**Si**	**TP**	**T N**	**T C**	**IC**	**OC**	**S**	**Si/Al**	**C/N**
1	213.70	228.15	0.65	0.58	10.85	2.75	8.11	7.35	1.07	18.86
1A	232.88	264.44	0.90	0.40	4.60	2.89	1.71	7.23	1.14	11.46
2	139.73	217.78	0.93	0.17	15.58	4.21	11.36	7.17	1.56	92.38
4	213.01	186.67	0.91	2.84	17.16	4.56	12.60	7.12	0.88	6.03
6	182.88	300.74	0.71	1.10	19.56	4.20	15.36	7.30	1.64	17.80
7	220.55	202.22	0.81	0.28	15.48	4.51	10.98	7.11	0.92	54.34
7A	229.45	248.89	0.70	0.90	16.07	4.23	11.84	7.21	1.08	17.95
7B	224.66	269.63	0.68	2.52	11.61	4.07	7.55	7.28	1.20	4.60
8	171.23	264.44	0.70	1.24	18.48	5.83	12.65	7.29	1.54	14.85
9	147.26	228.15	0.81	1.19	13.58	5.43	8.15	7.17	1.55	11.45
10	234.25	280.00	0.81	0.95	14.56	4.32	10.24	7.27	1.20	15.27
11	130.14	222.96	0.66	1.19	15.95	4.29	11.65	7.14	1.71	13.44
Min	130.14	186.67	0.65	0.17	4.60	2.75	1.71	7.11	0.88	4.60
Max	234.25	300.74	0.93	2.84	19.56	5.83	15.36	7.35	1.71	92.38
Mean	194.98	242.84	0.77	1.11	14.46	4.27	10.18	7.22	1.29	23.20
SD	38.87	33.95	0.10	0.82	4.00	0.86	3.48	0.08	0.29	25.18

core 1

	Al	**Si**	**P**	**T N**	**TC**	**IC**	**OC**	**S**	**Si/Al**	**C/N**
0_5	105.48	145.18	0.790	0.517	8.320	1.976	6.344	6.976	1.376	16.079
5_10	140.41	124.44	0.766	2.320	7.429	2.759	4.670	7.000	0.886	3.202
10_15	189.73	305.93	0.735	0.430	8.894	2.259	6.635	6.991	1.612	20.673
15_20	282.19	326.67	0.773	0.605	8.390	2.300	6.090	6.939	1.158	13.876
20_25	193.84	114.07	0.819	0.227	8.860	3.190	5.670	6.972	0.589	39.075
25_30	158.90	103.70	0.850	0.314	9.946	3.696	6.250	6.983	0.653	31.680
30_35	167.81	285.18	0.810	0.198	9.990	1.930	8.060	8.934	1.699	50.538
35_40	123.29	181.48	0.762	0.285	9.898	1.895	8.003	9.193	1.472	34.744

core 2

	Al	**Si**	**P**	**Kjha, N**	**TC**	**IC**	**OC**	**S**	**Si/Al**	**C/N**
0_5	116.44	119.26	0.986	1.302	31.980	4.338	27.642	7.180	1.024	24.556
5_10	105.48	171.11	0.926	3.395	26.865	2.384	24.481	7.097	1.622	7.912
10_15	164.38	186.67	0.974	2.610	29.629	3.239	26.390	7.010	1.136	11.350
15_20	124.66	160.74	0.977	2.203	25.188	5.452	19.736	7.092	1.289	11.431
20_25	132.19	171.11	0.977	0.576	22.642	3.530	19.112	7.071	1.294	39.338
25_30	183.56	150.37	0.990	0.866	39.295	4.198	35.097	10.116	0.819	45.361
30_35	186.30	172.59	0.883	0.837	28.876	8.732	20.144	6.992	0.926	34.491
35_40	154.79	207.41	0.974	7.116	24.786	4.560	20.226	7.017	1.340	3.483
40_45	229.45	233.33	0.984	1.215	36.575	2.176	34.399	9.370	1.017	30.100
45_50	141.78	222.96	0.629	1.012	51.794	4.339	47.455	16.950	1.573	51.199

core 3

	Al	**Si**	**P**	**Kjha, N**	**TC**	**IC**	**OC**	**S**	**Si/Al**	**C/N**
0_5	195.21	202.22	0.800	0.808	8.030	3.425	4.605	7.084	1.036	9.936
5_10	117.12	167.41	0.629	0.285	8.589	5.105	3.484	7.328	1.429	30.149
10_15	160.96	202.22	0.674	0.634	7.953	1.616	6.337	7.281	1.256	12.550
15_20	130.82	207.41	0.826	0.837	8.410	1.992	6.418	7.521	1.585	10.045
20_25	195.21	182.96	0.649	0.198	10.051	5.440	4.611	7.184	0.937	50.846
25_30	141.10	274.81	0.877	2.640	12.349	7.584	4.765	8.490	1.948	4.678
30_35	132.74	160.74	0.695	1.360	14.788	3.739	11.049	8.918	1.211	10.870
35_40	164.38	321.48	0.784	0.343	17.069	3.808	13.261	8.925	1.956	49.760

Appendix 3 Grain size control on nutrient distibution

Organic Carbon

	1	**6**	**7**	**8**	**9**	**10**
>125	18.185	5.484	2.339	7.954	1.107	2.946
<125-63>	3.379	13.984	5.473	2.492	4.208	6.341
<63-10>	2.620	22.051	6.268	6.342	3.398	4.463
<10	11.691	24.150	11.925	18.106	13.457	24.908

Sulfer

	1	**6**	**7**	**8**	**9**	**10**
>125	5.430	7.049	5.463	6.744	5.569	7.707
<125-63>	7.448	7.473	6.868	6.827	6.741	6.798
<63-10>	8.204	8.674	6.922	6.906	7.210	7.366
<10	9.330	8.381	8.440	6.987	17.189	7.854

Total Carbon

	1	**6**	**7**	**8**	**9**	**10**
>125	20.722	7.430	3.835	17.797	3.946	5.317
<125-63>	4.670	16.611	6.763	12.047	8.540	8.141
<63-10>	5.215	25.353	9.464	9.310	5.690	13.773
<10	20.125	25.797	20.462	20.722	20.930	26.555

Total P

	1	**6**	**7**	**8**	**9**	**10**
>125	0.774	0.484	0.726	1.016	0.774	1.016
<125-63>	0.726	0.726	0.822	0.822	0.822	0.339
<63-10>	0.629	1.112	0.484	0.580	0.339	1.112
<10	0.726	0.726	1.064	0.726	1.298	0.919

Total, N

	1	**6**	**7**	**8**	**9**	**10**
>125	0.69	2.35	0.78	2.26	0.69	0.66
<125-63>	0.84	2.96	0.87	1.01	0.31	0.69
<63-10>	1.07	2.38	0.90	0.98	0.95	1.24
<10	6.51	3.86	1.07	5.72	1.91	2.20

C/N Ratio

	1	**6**	**7**	**8**	**9**	**10**
>125	29.951	3.163	4.923	7.869	5.703	8.022
<125-63>	5.578	5.613	7.807	11.909	27.201	11.767
<63-10>	4.875	10.662	10.570	9.475	5.968	11.070
<10	3.093	6.682	19.128	3.622	10.942	12.051

Appendix 4 Phosphorus speciation in post tsunami sediments

phosphorus speciation conc(*10^3mico gram/gm)

	Adsorbed P	**Oxide bound P**	**Authigenic P**	**Detrital P**	**Organic P**	**sum**
1	0.016	0.139	0.202	0.198	0.098	0.653
1A	0.024	0.233	0.210	0.223	0.212	0.902
2	0.015	0.419	0.178	0.213	0.102	0.927
4	0.017	0.235	0.143	0.270	0.248	0.915
6	0.031	0.201	0.158	0.116	0.202	0.709
7	0.022	0.381	0.153	0.109	0.148	0.814
7A	0.043	0.311	0.143	0.154	0.048	0.698
7B	0.032	0.117	0.183	0.200	0.145	0.677
8	0.036	0.274	0.176	0.072	0.145	0.704
9	0.044	0.206	0.121	0.148	0.290	0.810
10	0.019	0.264	0.159	0.128	0.242	0.811
11	0.036	0.139	0.164	0.171	0.145	0.656
Min	**0.015**	**0.117**	**0.121**	**0.072**	**0.048**	**0.653**
Max	**0.044**	**0.419**	**0.210**	**0.270**	**0.290**	**0.927**
Mean	**0.028**	**0.243**	**0.166**	**0.167**	**0.169**	**0.773**
SD	**0.010**	**0.094**	**0.025**	**0.056**	**0.071**	**0.103**
Core 1	**Adsorbed P**	**Oxide bound P**	**Authigenic P**	**Detrital P**	**Organic P**	
0_5	0.033	0.252	0.155	0.102	0.248	0.790
5_10	0.033	0.266	0.161	0.074	0.232	0.766
10_15	0.027	0.243	0.168	0.061	0.235	0.735
15_20	0.019	0.268	0.166	0.074	0.247	0.773
20_25	0.024	0.280	0.180	0.061	0.273	0.819
25_30	0.039	0.286	0.178	0.066	0.282	0.850
30_35	0.039	0.249	0.170	0.062	0.290	0.810
35_40	0.022	0.220	0.164	0.053	0.302	0.762
Core 3	**Adsorbed P**	**Oxide bound P**	**Authigenic P**	**Detrital P**	**Organic P**	
0_5	0.024	0.315	0.170	0.094	0.197	0.800
5_10	0.016	0.279	0.129	0.060	0.145	0.629
10_15	0.012	0.194	0.159	0.071	0.239	0.674
15_20	0.022	0.262	0.172	0.075	0.293	0.826
20_25	0.026	0.091	0.166	0.075	0.290	0.649
25_30	0.015	0.321	0.161	0.084	0.297	0.877
30_35	0.013	0.134	0.170	0.070	0.308	0.695
35_40	0.011	0.285	0.139	0.051	0.297	0.784

Appendics 5 Grain size control on metal variation in post tsunami sediments

		Metal Concentration in μg/g							
Grain size	**Sample**	**Cd**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
<10	**1**	21	574	206	29780	640	194	181	146
	7	35	189	1127	29760	676	183	219	145
	8	26	189	1053	30880	1963	340	155	153
	9	11	738	171	30140	1138	244	194	179
	10	39	250	118	31920	998	206	245	173
	6	24	234	74	31390	1538	183	181	169
<63-10>	**1**	18	240	48	27790	992	206	116	89
	7	43	167	70	25810	634	107	181	109
	8	34	167	136	28480	970	229	103	142
	9	16	157	57	29600	892	118	90	139
	10	20	285	79	25720	772	198	191	126
	6	44	160	65	28320	1071	382	207	142
<125-63>	**1**	42	695	125	30990	3893	531	142	84
	7	14	247	148	28710	752	145	168	136
	8	59	247	92	29310	777	217	232	104
	9	28	183	67	26150	1023	108	181	109
	10	19	186	43	24020	802	179	181	85
	6	13	321	22	25850	892	164	116	100
>125	**1**	38	759	1352	28340	3521	5227	124	61
	7	18	286	1200	30750	863	2230	172	152
	8	24	286	180	27513	2131	4508	142	138
	9	31	186	96	29750	1093	2830	159	89
	10	23	196	2571	34810	905	1173	194	92
	6	12	366	136	19680	559	191	207	170

Appendix 6 Concentraion of Metals (µg/g) in post tsunami sediments

	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
1	35.74	634.00	88.24	24191.58	968.00	160.12	138.68	109.60
1A	31.00	458.00	100.36	20104.50	653.36	132.00	183.14	74.00
2	35.85	544.10	101.73	24923.74	632.04	143.90	162.54	140.50
4	36.44	565.99	168.42	25071.39	424.64	240.10	173.22	88.91
6	41.77	340.15	107.40	24926.34	723.31	219.53	119.30	114.99
7	32.80	885.46	183.47	27600.00	1111.19	543.00	131.78	114.70
7A	24.00	611.00	267.00	33380.00	1443.00	171.00	103.00	107.00
7B	13.00	286.00	170.00	22640.00	1513.00	91.00	174.00	72.00
8	34.85	706.00	188.68	25092.80	790.00	567.95	139.88	132.27
9	30.72	851.87	175.90	27400.00	1108.26	174.00	148.50	105.40
10	39.35	474.00	110.53	24900.00	692.00	153.00	138.93	78.33
11	28.86	711.64	98.70	25773.58	911.00	187.50	132.22	101.58
Min	13.00	286.00	88.24	20104.50	424.64	91.00	103.00	72.00
MaX	41.77	885.46	267.00	33380.00	1513.00	567.95	183.14	140.50
Mean	32.03	589.02	146.70	25500.33	914.15	231.92	145.43	103.27
SD	7.65	184.61	54.10	3170.36	331.13	156.07	23.88	21.78

Core 1

	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
0_5	32.16	329.55	121.01	30058.54	501.06	190.84	159.23	103.94
5_10	35.37	439.83	182.17	30165.36	653.02	299.37	180.81	135.49
10_15	28.79	434.30	263.32	31492.24	506.66	596.27	154.11	98.11
15_20	27.64	359.55	215.12	31579.96	1126.31	243.45	145.35	123.97
20_25	36.16	356.06	118.58	31693.97	1284.10	246.27	184.86	121.89
25_30	38.26	465.23	297.84	31296.68	1260.91	365.30	158.82	129.62
30_35	32.30	517.41	379.84	27927.04	1220.19	442.27	170.42	114.63
35_40	34.31	356.55	73.24	24584.07	743.85	281.21	156.92	83.42

Core 2

	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
0_5	27.45	529.92	102.76	28505.00	575.40	133.95	231.93	227.88
5_10	19.54	564.94	170.00	31715.15	595.84	229.65	194.66	156.36
10_15	20.73	275.34	113.51	29841.56	514.80	161.90	170.56	160.09
15_20	17.19	590.26	151.48	28152.39	616.48	275.93	207.53	138.90
20_25	33.97	664.70	211.53	31569.87	732.57	254.29	204.60	157.48
25_30	25.34	408.31	154.51	35334.32	616.55	279.20	219.75	130.02
30_35	26.61	421.30	194.04	31115.74	518.60	308.34	180.49	225.62
35_40	26.73	191.55	169.67	29297.40	390.15	197.88	185.46	128.40
40-45	28.34	410.31	206.57	31314.87	342.93	141.74	176.34	133.69
45-50	37.70	413.05	217.06	28374.40	601.48	200.85	208.43	126.64

Core 3

	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
0_5	33.64	472.32	166.32	27443.99	829.29	243.26	201.79	95.47
5_10	33.41	869.86	324.34	26498.02	862.77	321.67	187.76	116.32
10_15	38.72	872.92	157.58	32350.31	974.33	405.68	200.23	141.80
15_20	40.66	788.03	113.57	29594.10	625.02	492.43	221.59	144.42
20_25	38.26	607.08	192.79	35002.46	685.10	324.49	179.32	140.99
25_30	40.72	303.38	106.02	27901.69	401.26	166.36	179.69	235.75
30_35	36.58	408.90	167.02	29088.04	341.92	235.31	198.66	231.50
35_40	44.13	274.31	154.09	30670.85	323.69	193.35	209.22	244.38

Appendix 7 Speciation of Cd in post tsunami sediments

Cd

	Exch.	Carbonate	Fe-Mn	Organic	Residual	Σ speciation	Total	
1	0.20	0.21	0.44	0.64	31.00	32.49	35.74	Under Recovery
1A	0.20	0.23	0.54	0.64	27.00	28.61	31.00	Under Recovery
2	0.22	0.20	0.54	0.74	32.00	33.70	35.85	Under Recovery
4	0.28	0.22	0.62	0.76	29.00	30.88	36.44	Under Recovery
6	0.17	0.20	0.56	0.62	35.00	36.55	41.77	Under Recovery
7	0.18	0.22	0.58	0.54	28.00	29.51	32.80	Under Recovery
8	0.20	0.18	0.62	0.70	32.00	33.70	34.85	Under Recovery
9	0.22	0.20	0.38	0.64	26.00	27.44	30.72	Under Recovery
10	0.22	0.23	0.54	0.70	36.70	38.40	39.35	Under Recovery
11	0.22	0.22	0.58	0.70	24.00	25.71	28.86	Under Recovery
Min	**0.17**	**0.18**	**0.38**	**0.54**	**24.00**	**25.71**	**28.86**	
MaX	**0.28**	**0.23**	**0.62**	**0.76**	**36.70**	**38.40**	**41.77**	
Mean	**0.21**	**0.21**	**0.54**	**0.67**	**30.07**	**31.70**	**34.74**	
SD	**0.03**	**0.02**	**0.08**	**0.06**	**4.01**	**4.03**	**4.01**	
CORE 1	**Exch.**	**Carb**	**Fe-Mn**	**Organic**	**Residual**	**Σ speciation**	**Total (Bulk)**	
0_5	0.18	0.15	0.38	0.62	28.00	29.33	32.16	Under Recovery
5_10	1.44	0.20	0.36	0.74	31.00	33.74	35.37	Under Recovery
10_15	0.21	0.22	0.42	0.72	25.00	26.57	28.79	Under Recovery
15_20	0.24	0.22	0.48	0.34	24.00	25.28	27.64	Under Recovery
20_25	0.22	0.26	0.36	0.48	32.00	33.32	36.16	Under Recovery
25_30	0.19	0.23	0.38	0.72	34.00	35.52	38.26	Under Recovery
30_35	0.40	0.14	0.48	0.58	31.00	32.60	32.30	Over Recovery
35_40	0.43	0.26	0.32	0.62	30.00	31.63	34.31	Under Recovery
average	**0.41**	**0.21**	**0.40**	**0.60**	**29.38**	**31.00**	**33.12**	
CORE 2	**Exch.**	**Carb**	**Fe-Mn**	**Organic**	**Residual**	**Σ speciation**	**Total (Bulk)**	
0_5	0.23	0.18	0.76	0.74	24.00	25.91	27.45	Under Recovery
5_10	0.19	0.14	0.06	0.70	17.00	18.09	19.54	Under Recovery
10_15	0.07	0.17	0.58	0.64	18.00	19.46	20.73	Under Recovery
15_20	0.16	0.14	0.32	0.76	13.00	14.38	17.19	Under Recovery
20_25	0.45	0.07	0.48	0.94	29.00	30.94	33.97	Under Recovery
25_30	0.21	0.20	0.64	0.64	22.00	23.69	25.34	Under Recovery
30_35	0.10	0.18	0.34	0.60	22.00	23.23	26.61	Under Recovery
35_40	0.18	0.07	0.22	1.00	24.00	25.47	26.73	Under Recovery
40-45	0.30	0.20	0.24	0.94	25.00	26.68	28.34	Under Recovery
45-50	0.28	0.12	0.26	0.74	32.00	33.40	37.70	Under Recovery
average	**0.22**	**0.15**	**0.39**	**0.77**	**22.60**	**24.12**	**26.36**	
CORE 3	**Exch.**	**Carb**	**Fe-Mn**	**Organic**	**Residual**	**Σ speciation**	**Total (Bulk)**	
0_5	0.15	0.14	0.28	0.72	29.00	30.29	33.64	Under Recovery
5_10	0.18	0.14	0.30	0.76	31.00	32.39	33.41	Under Recovery
10_15	0.14	0.23	0.34	0.74	32.00	33.45	38.72	Under Recovery
15_20	0.13	0.18	0.26	0.74	33.00	34.31	40.66	Under Recovery
20_25	0.10	0.18	0.38	0.86	31.00	32.52	38.26	Under Recovery
25_30	0.23	0.22	0.22	0.78	36.00	37.45	40.72	Under Recovery
30_35	0.33	0.14	0.36	0.34	34.00	35.16	36.58	Under Recovery
35_40	0.26	0.26	0.34	0.40	38.00	39.26	44.13	Under Recovery
average	**0.19**	**0.19**	**0.31**	**0.67**	**33.00**	**34.35**	**38.27**	

Appendix 8 Speciation of Cr in post tsunami sediments

Cr

	Exch.	Carbonate	Fe-Mn	Organic	Residual	Σ speciation	Total	
1	0.28	0.69	5.20	13.94	586.00	606.11	634.00	Under Recovery
1A	0.18	0.87	3.66	6.88	424.00	435.59	458.00	Under Recovery
2	0.28	0.43	4.56	16.92	478.00	500.19	544.10	Under Recovery
4	0.26	0.77	3.90	22.06	508.00	534.98	565.99	Under Recovery
6	0.13	0.94	3.98	19.24	280.00	304.29	340.15	Under Recovery
7	0.22	0.69	3.40	15.60	762.00	781.91	885.46	Under Recovery
8	0.30	0.64	3.58	18.50	605.00	628.02	706.00	Under Recovery
9	0.46	0.41	3.66	7.22	702.00	713.74	851.87	Under Recovery
10	0.30	0.85	3.58	12.60	385.00	402.33	474.00	Under Recovery
11	0.41	0.85	4.56	7.46	614.00	627.28	711.64	Under Recovery
Min	**0.13**	**0.41**	**3.40**	**6.88**	**280.00**	**304.29**	**340.15**	
MaX	**0.46**	**0.94**	**5.20**	**22.06**	**762.00**	**781.91**	**885.46**	
Mean	**0.28**	**0.71**	**4.01**	**14.04**	**534.40**	**553.45**	**617.12**	
SD	**0.10**	**0.18**	**0.58**	**5.43**	**147.94**	**146.69**	**174.70**	

CORE 1	**Exch.**	**Carb**	**Fe-Mn**	**Organic**	**Residual**	**Σ speciation**	**Total (Bulk)**	
0_5	0.72	0.58	5.46	14.34	290.00	311.10	329.55	Under Recovery
5_10	0.66	0.74	6.34	18.92	394.00	420.66	439.83	Under Recovery
10_15	1.28	0.43	5.12	16.76	379.00	402.59	434.30	Under Recovery
15_20	1.07	0.58	7.70	19.74	321.00	350.10	359.55	Under Recovery
20_25	1.02	2.48	6.86	15.76	321.00	347.12	356.06	Under Recovery
25_30	0.10	0.28	6.68	20.40	395.00	422.46	465.23	Under Recovery
30_35	0.35	0.46	6.68	18.34	482.00	507.83	517.41	Under Recovery
35_40	0.19	0.66	4.56	14.68	311.00	331.10	356.55	Under Recovery
average	**0.67**	**0.78**	**6.18**	**17.37**	**361.63**	**386.62**	**407.31**	

CORE 2	**Exch.**	**Carb**	**Fe-Mn**	**Organic**	**Residual**	**Σ speciation**	**Total (Bulk)**	
0_5	0.06	1.05	8.86	25.88	425.00	460.84	529.92	Under Recovery
5_10	0.10	0.69	3.52	23.58	513.00	540.88	564.94	Under Recovery
10_15	0.18	0.77	3.26	22.48	228.00	254.68	275.34	Under Recovery
15_20	0.13	0.71	11.24	54.44	487.00	553.52	590.26	Under Recovery
20_25	0.22	0.62	7.18	25.38	566.00	599.40	664.70	Under Recovery
25_30	0.10	0.82	6.28	19.42	373.00	399.61	408.31	Under Recovery
30_35	0.36	0.98	4.30	26.96	360.00	392.60	421.30	Under Recovery
35_40	0.17	0.92	3.90	33.10	124.00	162.09	191.55	Under Recovery
40-45	0.14	1.02	3.00	28.46	332.00	364.62	410.31	Under Recovery
45-50	0.46	1.05	5.20	21.40	404.00	432.10	413.05	Under Recovery
average	**0.19**	**0.86**	**5.67**	**28.11**	**381.20**	**416.04**	**446.97**	

CORE 3	**Exch.**	**Carb**	**Fe-Mn**	**Organic**	**Residual**	**Σ speciation**	**Total (Bulk)**	
0_5	0.41	0.28	6.86	15.10	425.00	447.65	472.32	Under Recovery
5_10	0.43	0.43	4.36	19.50	745.00	769.72	869.86	Under Recovery
10_15	0.30	0.51	4.94	19.08	769.00	793.84	872.92	Under Recovery
15_20	0.07	0.77	3.72	18.50	665.00	688.06	788.03	Under Recovery
20_25	0.30	0.38	4.30	13.18	511.00	529.17	607.08	Under Recovery
25_30	0.26	0.64	8.80	22.06	238.00	269.76	303.38	Under Recovery
30_35	0.33	0.79	6.16	31.52	321.00	359.80	408.90	Under Recovery
35_40	0.28	1.15	3.34	16.84	218.00	239.61	274.31	Under Recovery
average	**0.30**	**0.62**	**5.31**	**19.47**	**486.50**	**512.20**	**574.60**	

Appendix 9 Speciation of Cu in post tsunami sediments

Cu

	Exch.	Carbonate	Fe-Mn	Organic	Residual	Σ speciation	Total	
1	0.36	0.95	1.48	3.68	78.00	84.47	88.24	Under Recovery
1A	0.45	1.43	1.88	0.96	79.00	83.72	100.36	Under Recovery
2	0.43	2.29	10.60	6.14	79.00	98.46	101.73	Under Recovery
4	0.68	2.66	2.54	5.96	130.00	141.84	168.42	Under Recovery
6	0.61	1.10	2.74	7.28	81.00	92.73	107.40	Under Recovery
7	0.32	1.67	2.96	2.98	143.00	150.93	183.47	Under Recovery
8	0.61	1.60	4.22	3.94	157.00	167.37	188.68	Under Recovery
9	0.27	0.90	4.10	3.96	142.00	151.23	175.90	Under Recovery
10	0.58	1.12	2.92	2.44	76.00	83.06	110.53	Under Recovery
11	0.42	1.22	2.48	1.30	76.00	81.43	98.70	Under Recovery
Min	**0.27**	**0.90**	**1.48**	**0.96**	**76.00**	**81.43**	**88.24**	
MaX	**0.68**	**2.66**	**10.60**	**7.28**	**157.00**	**167.37**	**188.68**	
Mean	**0.47**	**1.50**	**3.59**	**3.86**	**104.10**	**113.52**	**132.34**	
SD	**0.14**	**0.58**	**2.61**	**2.08**	**34.11**	**34.76**	**40.99**	

CORE 1	Exch.	Carb	Fe-Mn	Organic	Residual	Σ speciation	Total (Bulk)	
0_5	1.01	1.38	5.68	3.94	103.00	115.01	121.01	Under Recovery
5_10	1.15	1.21	6.94	6.04	157.00	172.34	182.17	Under Recovery
10_15	1.50	0.97	5.54	5.62	209.00	222.63	263.32	Under Recovery
15_20	1.49	1.44	10.00	6.32	193.00	212.25	215.12	Under Recovery
20_25	0.24	1.69	10.90	6.34	74.00	93.17	118.58	Under Recovery
25_30	0.22	2.14	7.12	60.20	191.00	260.68	297.84	Under Recovery
30_35	0.27	2.14	5.04	11.24	340.00	358.69	379.84	Under Recovery
35_40	0.21	2.10	3.82	8.34	36.00	50.47	73.24	Under Recovery
average	**0.76**	**1.63**	**6.88**	**13.51**	**162.88**	**185.66**	**206.39**	

CORE 2	Exch.	Carb	Fe-Mn	Organic	Residual	Σ speciation	Total (Bulk)	
0_5	1.47	3.81	1.30	16.94	54.00	77.52	102.76	Under Recovery
5_10	0.84	4.00	2.60	14.94	142.00	164.38	170.00	Under Recovery
10_15	0.68	4.38	2.24	10.72	83.00	101.02	113.51	Under Recovery
15_20	0.55	3.50	2.84	14.06	115.00	135.96	151.48	Under Recovery
20_25	0.75	2.22	5.86	20.24	153.00	182.07	211.53	Under Recovery
25_30	0.70	4.81	9.28	23.24	105.00	143.02	154.51	Under Recovery
30_35	1.06	4.49	3.68	18.34	124.00	151.57	194.04	Under Recovery
35_40	1.74	7.74	3.82	22.04	103.00	138.34	169.67	Under Recovery
40-45	2.09	6.70	1.20	44.16	121.00	175.14	206.57	Under Recovery
45-50	2.03	2.29	0.90	42.90	146.00	194.12	217.06	Under Recovery
average	**1.19**	**4.39**	**3.37**	**22.76**	**114.60**	**146.31**	**169.11**	

CORE 3	Exch.	Carb	Fe-Mn	Organic	Residual	Σ speciation	Total (Bulk)	
0_5	0.12	1.46	5.32	3.74	133.00	143.64	166.32	Under Recovery
5_10	0.10	1.83	6.04	7.70	234.00	249.68	324.34	Under Recovery
10_15	0.22	1.76	5.98	7.20	117.00	132.16	157.58	Under Recovery
15_20	0.54	1.87	4.94	5.80	87.00	100.15	113.57	Under Recovery
20_25	0.50	2.22	7.20	6.66	133.00	149.58	192.79	Under Recovery
25_30	0.90	2.90	5.44	27.80	47.00	84.03	106.02	Under Recovery
30_35	1.10	2.66	5.88	33.40	90.00	133.04	167.02	Under Recovery
35_40	1.66	2.34	6.40	52.78	58.00	121.18	154.09	Under Recovery
average	**0.64**	**2.13**	**5.90**	**18.14**	**112.38**	**139.18**	**172.72**	

Appendix 10 Speciation of Fe in post tsunami sediments

Fe

	Exch.	Carbonate	Fe-Mn	Organic	Residual	Σ speciation	Total	Remarks
1	14.39	80.72	975.60	695.40	21400.00	23166.11	24191.58	Under Recovery
1A	17.64	83.36	848.60	425.40	17090.00	18465.00	20104.50	Under Recovery
2	12.44	129.84	984.60	721.60	22080.00	23928.48	24923.74	Under Recovery
4	13.42	100.16	993.80	687.40	22060.00	23854.78	25071.39	Under Recovery
6	11.23	219.84	957.60	704.00	21400.00	23292.67	24926.34	Under Recovery
7	11.56	74.52	938.20	646.80	24140.00	25811.08	27600.00	Under Recovery
8	13.16	39.45	943.40	661.60	20400.00	22057.61	25092.80	Under Recovery
9	12.46	121.68	844.00	634.20	21730.00	23342.34	27400.00	Under Recovery
10	16.80	146.56	957.40	614.00	21750.00	23484.76	24900.00	Under Recovery
11	24.45	135.52	886.40	510.80	21900.00	23457.17	25773.58	Under Recovery
Min	**11.23**	**39.45**	**844.00**	**425.40**	**17090.00**	**18465.00**	**20104.50**	
MaX	**24.45**	**219.84**	**993.80**	**721.60**	**24140.00**	**25811.08**	**27600.00**	
Mean	**14.75**	**113.16**	**932.96**	**630.12**	**21395.00**	**23086.00**	**24998.39**	
SD	**4.00**	**49.87**	**54.49**	**93.73**	**1778.35**	**1872.30**	**2048.65**	

CORE 1	**Exch.**	**Carb**	**Fe-Mn**	**Organic**	**Residual**	**Σ speciation**	**Total (Bulk)**	
0_5	0.90	13.78	900.40	662.00	25020.00	26597.08	30058.54	Under Recovery
5_10	1.98	16.54	998.80	683.40	25050.00	26750.72	30165.36	Under Recovery
10_15	1.79	13.70	900.80	688.20	27370.00	28974.48	31492.24	Under Recovery
15_20	1.65	14.07	923.80	690.40	25930.00	27559.92	31579.96	Under Recovery
20_25	2.78	13.95	959.60	681.60	26850.00	28507.94	31693.97	Under Recovery
25_30	1.14	19.42	994.80	698.00	26720.00	28433.36	31296.68	Under Recovery
30_35	1.31	37.77	963.40	751.60	23700.00	25454.08	27927.04	Under Recovery
35_40	3.12	57.82	977.00	730.20	21190.00	22958.14	24584.07	Under Recovery
AVERAGE	**1.83**	**23.38**	**952.33**	**698.18**	**25228.75**	**26904.46**	**29849.73**	

CORE 2	**Exch.**	**Carb**	**Fe-Mn**	**Organic**	**Residual**	**Σ speciation**	**Total (Bulk)**	
0_5	0.33	258.08	964.60	767.00	22500.00	24490.01	28505.00	Under Recovery
5_10	1.06	212.64	995.20	691.40	25810.00	27710.30	31715.15	Under Recovery
10_15	0.47	240.64	993.00	689.00	26070.00	27993.11	29841.56	Under Recovery
15_20	0.50	176.08	993.60	684.60	24690.00	26544.78	28152.39	Under Recovery
20_25	0.54	77.39	932.80	659.00	26090.00	27759.74	31569.87	Under Recovery
25_30	2.67	192.96	902.20	700.80	26550.00	28348.63	35334.32	Under Recovery
30_35	8.83	210.64	905.40	676.60	26010.00	27811.47	31115.74	Under Recovery
35_40	2.57	178.24	981.60	662.40	25820.00	27644.81	29297.40	Under Recovery
40-45	7.46	117.68	948.40	756.20	26970.00	28799.74	31314.87	Under Recovery
45-50	8.12	218.48	918.00	844.20	25140.00	27128.80	28374.40	Under Recovery
average	**3.26**	**188.28**	**953.48**	**713.12**	**25565.00**	**27423.14**	**30522.07**	

CORE 3	**Exch.**	**Carb**	**Fe-Mn**	**Organic**	**Residual**	**Σ speciation**	**Total (Bulk)**	
0_5	1.04	61.14	957.80	668.00	23330.00	25017.98	27443.99	Under Recovery
5_10	0.99	50.66	934.80	679.60	22310.00	23976.05	26498.02	Under Recovery
10_15	0.82	28.40	931.80	679.60	28220.00	29860.62	32350.31	Under Recovery
15_20	0.30	60.09	999.40	688.40	25110.00	26858.19	29594.10	Under Recovery
20_25	0.11	98.80	931.80	674.20	29950.00	31654.91	35002.46	Under Recovery
25_30	0.30	91.68	901.60	689.80	24130.00	25813.38	27901.69	Under Recovery
30_35	1.16	196.32	959.00	709.60	24360.00	26226.08	29088.04	Under Recovery
35_40	3.95	196.16	910.00	821.60	25730.00	27661.71	30670.85	Under Recovery
average	**1.08**	**97.91**	**940.78**	**701.35**	**25392.50**	**27133.61**	**29818.68**	

Appendix 11 Speciation of Mn in post tsunami sediments

Mn

	Exch.	Carbonate	Fe-Mn	Organic	Residual	Σ speciation	Total	
1	19.26	4.81	12.08	19.18	783.00	838.33	968.00	Under Recovery
1A	8.61	17.11	10.96	6.04	562.00	604.72	653.36	Under Recovery
2	54.01	80.56	45.14	41.38	374.00	595.09	632.04	Under Recovery
4	14.07	11.27	16.22	16.72	296.00	354.28	424.64	Under Recovery
6	71.65	151.60	58.90	38.48	383.00	703.63	723.31	Under Recovery
7	34.34	65.94	55.42	34.68	912.00	1102.38	1111.19	Under Recovery
8	46.47	21.94	179.84	112.88	321.00	682.14	790.00	Under Recovery
9	15.32	23.46	11.86	6.88	961.00	1018.52	1108.26	Under Recovery
10	36.71	34.43	25.78	12.74	492.00	601.66	692.00	Under Recovery
11	4.87	23.38	13.92	12.12	827.00	881.29	911.00	Under Recovery
Min	**4.87**	**4.81**	**10.96**	**6.04**	**296.00**	**354.28**	**424.64**	
MaX	**71.65**	**151.60**	**179.84**	**112.88**	**961.00**	**1102.38**	**1111.19**	
Mean	**30.53**	**43.45**	**43.01**	**30.11**	**591.10**	**738.20**	**801.38**	
SD	**21.90**	**44.90**	**51.58**	**31.82**	**256.78**	**223.70**	**221.27**	

CORE 1	**Exch.**	**Carb**	**Fe-Mn**	**Organic**	**Residual**	**Σ speciation**	**Total (Bulk)**	
0_5	14.54	30.83	82.62	51.12	299.00	478.12	501.06	Under Recovery
5_10	15.12	21.48	85.14	84.30	318.00	524.04	653.02	Under Recovery
10_15	10.06	18.32	39.04	42.90	323.00	433.32	506.66	Under Recovery
15_20	28.54	44.08	372.60	198.40	369.00	1012.62	1126.31	Under Recovery
20_25	47.07	90.32	341.60	511.20	243.00	1233.19	1284.10	Under Recovery
25_30	13.82	18.90	76.18	77.92	983.00	1169.83	1260.91	Under Recovery
30_35	40.58	37.05	44.58	28.18	1026.00	1176.38	1220.19	Under Recovery
35_40	32.98	43.05	16.88	20.80	489.00	602.70	743.85	Under Recovery
average	**25.34**	**38.00**	**132.33**	**126.85**	**506.25**	**828.78**	**912.01**	Under Recovery

CORE 2	**Exch.**	**Carb**	**Fe-Mn**	**Organic**	**Residual**	**Σ speciation**	**Total (Bulk)**	
0_5	113.92	42.04	33.84	57.00	254.00	500.80	575.40	Under Recovery
5_10	53.04	55.98	36.18	46.48	316.00	507.68	595.84	Under Recovery
10_15	45.40	55.65	29.02	39.54	274.00	443.61	514.80	Under Recovery
15_20	73.43	28.54	56.38	92.62	327.00	577.97	616.48	Under Recovery
20_25	46.67	14.74	61.64	77.08	512.00	712.14	732.57	Under Recovery
25_30	36.94	26.42	139.06	107.68	251.00	561.10	616.55	Under Recovery
30_35	16.94	13.54	40.22	48.50	387.00	506.19	518.60	Under Recovery
35_40	37.72	16.94	26.50	47.14	232.00	360.30	390.15	Under Recovery
40-45	23.87	6.60	4.96	39.42	234.00	308.85	342.93	Under Recovery
45-50	22.13	8.48	11.74	96.60	383.00	521.95	601.48	Under Recovery
average	**47.01**	**26.89**	**43.95**	**65.21**	**317.00**	**500.06**	**550.48**	Under Recovery

CORE 3	**Exch.**	**Carb**	**Fe-Mn**	**Organic**	**Residual**	**Σ speciation**	**Total (Bulk)**	
0_5	53.38	122.88	128.26	58.06	450.00	812.58	829.29	Under Recovery
5_10	72.18	88.88	84.06	55.42	510.00	810.54	862.77	Under Recovery
10_15	78.60	105.84	111.60	75.62	590.00	961.66	974.33	Under Recovery
15_20	42.54	46.54	30.08	56.88	386.00	562.03	625.02	Under Recovery
20_25	34.61	52.25	28.92	38.42	490.00	644.20	685.10	Under Recovery
25_30	31.48	19.24	27.28	27.52	265.00	370.52	401.26	Under Recovery
30_35	16.51	10.18	16.38	24.78	204.00	271.85	341.92	Under Recovery
35_40	14.61	10.87	7.66	52.24	179.00	264.38	323.69	Under Recovery
average	**42.99**	**57.08**	**54.28**	**48.62**	**384.25**	**587.22**	**630.42**	

Appendix 12 Speciation of Ni in post tsunami sediments

Ni

	Exch.	Carbonate	Fe-Mn	Organic	Residual	Σ speciation	Total	
1	1.77	1.53	5.42	4.66	141.00	154.38	160.12	Under Recovery
1A	0.24	1.50	4.20	2.98	117.00	125.92	132.00	Under Recovery
2	0.70	1.74	4.20	9.16	125.00	140.79	143.90	Under Recovery
4	1.46	1.68	2.66	8.40	207.00	221.20	240.10	Under Recovery
6	0.46	2.32	5.34	8.94	182.00	199.06	219.53	Under Recovery
7	0.39	1.83	3.82	9.32	445.00	460.36	543.00	Under Recovery
8	0.86	2.41	6.34	12.30	408.00	429.90	567.95	Under Recovery
9	0.67	1.03	3.04	3.20	162.00	169.94	174.00	Under Recovery
10	1.37	2.02	4.42	5.64	133.00	146.44	153.00	Under Recovery
11	1.12	2.91	1.90	3.04	163.00	171.97	187.50	Under Recovery
Min	**0.24**	**1.03**	**1.90**	**2.98**	**117.00**	**125.92**	**132.00**	
MaX	**1.77**	**2.91**	**6.34**	**12.30**	**445.00**	**460.36**	**567.95**	
Mean	**0.90**	**1.90**	**4.13**	**6.76**	**208.30**	**222.00**	**252.11**	
SD	**0.51**	**0.54**	**1.35**	**3.28**	**118.45**	**121.06**	**163.39**	

CORE 1	Exch.	Carb	Fe-Mn	Organic	Residual	Σ speciation	Total (Bulk)	
0_5	4.21	1.43	6.34	7.70	152.00	171.68	190.84	Under Recovery
5_10	2.43	1.25	6.56	16.50	236.00	262.74	299.37	Under Recovery
10_15	1.89	1.06	3.42	10.16	554.00	570.53	596.27	Under Recovery
15_20	0.72	1.74	11.60	21.84	202.00	237.90	243.45	Under Recovery
20_25	0.85	2.07	15.36	17.26	194.00	229.54	246.27	Under Recovery
25_30	2.62	1.31	10.00	14.66	325.00	353.60	365.30	Under Recovery
30_35	1.71	4.30	10.84	12.68	359.00	388.54	442.27	Under Recovery
35_40	2.32	3.51	4.58	9.00	252.00	271.41	281.21	Under Recovery
average	**2.09**	**2.09**	**8.59**	**13.73**	**284.25**	**310.74**	**333.12**	

CORE 2	Exch.	Carb	Fe-Mn	Organic	Residual	Σ speciation	Total (Bulk)	
0_5	2.10	3.24	12.44	16.12	95.00	128.90	133.95	Under Recovery
5_10	1.22	3.24	4.72	15.12	187.00	211.30	229.65	Under Recovery
10_15	0.94	3.24	4.34	13.28	133.00	154.80	161.90	Under Recovery
15_20	0.36	3.00	12.68	73.82	168.00	257.86	275.93	Under Recovery
20_25	0.42	1.53	4.12	17.50	217.00	240.57	254.29	Under Recovery
25_30	1.31	2.81	7.86	16.42	145.00	173.40	279.20	Under Recovery
30_35	0.86	2.20	3.66	16.96	264.00	287.68	308.34	Under Recovery
35_40	1.16	2.57	4.42	21.62	133.00	162.77	197.88	Under Recovery
40-45	2.12	3.73	3.12	26.50	91.00	126.47	141.74	Under Recovery
45-50	2.13	3.08	4.66	25.82	145.00	180.69	200.85	Under Recovery
average	**1.26**	**2.86**	**6.20**	**24.32**	**157.80**	**192.44**	**218.37**	

CORE 3	Exch.	Carb	Fe-Mn	Organic	Residual	Σ speciation	Total (Bulk)	
0_5	0.91	2.41	5.88	8.32	210.00	227.52	243.26	Under Recovery
5_10	1.43	3.21	5.88	12.82	268.00	291.34	321.67	Under Recovery
10_15	1.55	3.58	5.88	14.36	363.00	388.37	405.68	Under Recovery
15_20	1.43	6.72	6.72	12.98	431.00	458.85	492.43	Under Recovery
20_25	1.06	7.91	6.10	13.90	240.00	268.98	324.49	Under Recovery
25_30	4.03	7.82	6.56	22.30	114.00	154.72	166.36	Under Recovery
30_35	2.69	5.96	12.68	22.30	122.00	165.63	235.31	Under Recovery
35_40	7.36	10.21	5.04	29.10	95.00	146.71	193.35	Under Recovery
average	**2.56**	**5.98**	**6.84**	**17.01**	**230.38**	**262.76**	**297.82**	

Appendix 13 Speciation of Pb in post tsunami sediments

Pb

	Exch.	Carb	Fe-Mn	Organic	Residual	Σ speciation	Total (Bulk)	Remarks
1	1.55	3.72	6.46	3.62	119.00	134.35	138.68	Under Recovery
1A	1.44	4.11	6.70	5.98	118.80	137.03	183.14	Under Recovery
2	1.66	3.72	5.42	8.28	129.00	148.08	162.54	Under Recovery
4	1.14	3.70	9.30	9.30	142.00	165.43	173.22	Under Recovery
6	1.75	4.86	7.24	8.28	92.00	114.14	119.30	Under Recovery
7	1.03	4.14	6.98	5.42	91.00	108.57	131.78	Under Recovery
8	1.96	4.03	9.56	6.20	103.00	124.75	139.88	Under Recovery
9	1.66	3.72	7.24	4.38	129.00	146.00	148.50	Under Recovery
10	1.86	4.34	6.98	5.68	117.00	135.86	138.93	Under Recovery
11	1.34	4.66	5.94	7.50	116.00	135.44	132.22	Over Recovery
Min	**1.03**	**3.70**	**5.42**	**3.62**	**91.00**	**108.57**	**119.30**	
MaX	**1.96**	**4.86**	**9.56**	**9.30**	**142.00**	**165.43**	**183.14**	
Mean	**1.54**	**4.10**	**7.18**	**6.46**	**115.68**	**134.96**	**146.82**	
SD	**0.30**	**0.42**	**1.32**	**1.83**	**16.33**	**16.54**	**20.11**	

CORE 1	**Exch.**	**Carb**	**Fe-Mn**	**Organic**	**Residual**	**Σ speciation**	**Total (Bulk)**	**Remarks**
0_5	3.31	4.03	15.00	12.12	135.00	169.46	159.23	Over Recovery
5_10	2.90	4.76	14.32	20.44	148.20	190.62	180.81	Over Recovery
10_15	3.50	3.93	14.48	15.00	132.30	169.21	154.11	Over Recovery
15_20	3.92	5.17	19.92	20.70	103.00	152.71	145.35	Over Recovery
20_25	2.69	3.42	20.18	20.44	155.00	201.72	184.86	Over Recovery
25_30	3.10	4.66	16.04	17.84	137.00	178.64	158.82	Over Recovery
30_35	3.31	6.00	12.92	10.60	129.00	161.83	170.42	Over Recovery
35_40	2.27	5.17	12.42	6.98	119.00	145.84	156.92	Under Recovery
AVERAGE	**3.13**	**4.64**	**15.66**	**15.52**	**132.31**	**171.25**	**163.81**	
CORE2	**Exch.**	**Carb**	**Fe-Mn**	**Organic**	**Residual**	**Σ speciation**	**Total (Bulk)**	
0_5	2.79	6.21	17.84	23.02	207.00	256.86	231.93	Over Recovery
5_10	3.00	4.76	17.84	20.72	142.00	188.32	194.66	Over Recovery
10_15	2.26	4.86	16.56	20.44	123.00	167.12	170.56	Under Recovery
15_20	2.38	4.10	14.74	17.84	177.00	216.05	207.53	Over Recovery
20_25	1.75	3.42	14.48	16.56	174.00	210.21	204.60	Over Recovery
25_30	2.17	3.62	20.70	23.02	187.00	236.50	219.75	Over Recovery
30_35	1.75	5.27	18.62	25.34	155.00	205.98	180.49	Over Recovery
35_40	1.66	5.79	13.18	16.30	142.00	178.93	165.46	Under Recovery
40-45	4.02	6.52	12.92	15.22	129.00	167.68	176.34	Under Recovery
45-50	8.18	5.38	15.26	15.04	176.80	220.65	208.43	Over Recovery
AVERAGE	**3.00**	**4.99**	**16.21**	**19.35**	**161.28**	**204.83**	**197.98**	
CORE 3	**Exch.**	**Carb**	**Fe-Mn**	**Organic**	**Residual**	**Σ speciation**	**Total (Bulk)**	
0_5	1.24	5.27	11.90	12.16	175.50	206.07	201.79	Over Recovery
5_10	1.75	4.76	13.96	16.04	167.00	203.51	187.76	Over Recovery
10_15	1.03	9.00	11.90	15.52	179.20	216.65	200.23	Over Recovery
15_20	1.66	5.17	14.22	19.14	185.00	225.18	221.59	Over Recovery
20_25	2.38	5.69	13.18	22.40	154.10	197.74	179.32	Over Recovery
25_30	2.27	6.42	15.52	13.18	132.10	169.49	179.69	Under Recovery
30_35	2.38	5.48	13.46	15.00	158.00	194.32	198.66	Under Recovery
35_40	4.34	5.07	10.38	11.64	162.00	193.44	209.22	Under Recovery
AVERAGE	**2.13**	**5.86**	**13.07**	**15.64**	**164.11**	**200.80**	**197.28**	

Appendix 14. Speciation of Zn in post tsunami sediments

Zn

	Exch.	Carbonate	Fe-Mn	Organic	Residual	Σ speciation	Total	
1	1.376	0.944	3.56	3.6	104	113.48	109.60	Under Recovery
1A	0.272	1.712	2.46	1.82	60	66.26	74.00	Under Recovery
2	0.392	2.568	4.12	4.92	106	118.00	140.50	Under Recovery
4	0.544	1.384	2.84	4.06	65	73.83	88.91	Under Recovery
6	0.232	2.448	4.98	5.32	92	104.98	114.99	Under Recovery
7	0.184	1.168	3.02	3.86	96	104.23	114.70	Under Recovery
8	0.176	1.544	4.68	4.14	102	112.54	132.27	Under Recovery
9	0.32	1.336	3.74	5.8	84	95.20	105.40	Under Recovery
10	0.576	1.496	3.92	2.66	66	74.65	78.33	Under Recovery
11	0.168	2.528	3.84	2.62	90	99.16	101.58	Under Recovery
Min	**0.17**	**0.94**	**2.46**	**1.82**	**60.00**	**66.26**	**74.00**	
MaX	**1.38**	**2.57**	**4.98**	**5.80**	**106.00**	**118.00**	**140.50**	
Mean	**0.42**	**1.71**	**3.72**	**3.88**	**86.50**	**96.23**	**106.03**	
SD	**0.37**	**0.59**	**0.79**	**1.26**	**17.16**	**18.42**	**21.48**	

CORE 1	Exch.	Carb	Fe-Mn	Organic	Residual	Σ speciation	Total (Bulk)	
0_5	0.368	0.816	4.54	4.16	87	96.88	103.94	Under Recovery
5_10	0.528	1.096	4.54	5.82	118	129.98	135.49	Under Recovery
10_15	0.56	0.92	4.14	5.6	80	91.22	98.11	Under Recovery
15_20	0.432	1.24	6.22	6.04	104	117.93	123.97	Under Recovery
20_25	0.56	1.464	7	5.76	101	115.78	121.89	Under Recovery
25_30	0.576	0.96	4.12	5.58	106	117.24	129.62	Under Recovery
30_35	0.56	2.192	5.18	7.32	90	105.25	114.63	Under Recovery
35_40	0.24	1.88	3.36	5.36	71	81.84	83.42	Under Recovery
average	**0.48**	**1.32**	**4.89**	**5.71**	**94.63**	**107.02**	**113.88**	

CORE 2	Exch.	Carb	Fe-Mn	Organic	Residual	Σ speciation	Total (Bulk)	
0_5	3.944	4.304	8.12	11.4	193	220.77	227.88	Under Recovery
5_10	1.344	4.224	6.1	7.06	104	122.73	156.36	Under Recovery
10_15	1.448	3.816	5.4	6.52	138	155.18	160.09	Under Recovery
15_20	0.488	2.216	6.36	9.74	112	130.80	138.90	Under Recovery
20_25	0.944	1.544	6.12	11.36	139	158.97	157.48	Under Recovery
25_30	1.144	2.72	9.06	13.12	100	126.04	130.02	Under Recovery
30_35	1.592	3.96	7.62	11.06	187	211.23	225.62	Under Recovery
35_40	7.912	10.736	9.74	10.42	80	118.81	128.40	Under Recovery
40-45	5.64	1.896	3.42	15.42	106	132.38	133.69	Under Recovery
45-50	7.232	2.384	5.48	17.18	91	123.28	126.64	Under Recovery
average	**3.17**	**3.78**	**6.74**	**11.33**	**125.00**	**150.02**	**158.51**	

CORE 3	Exch.	Carb	Fe-Mn	Organic	Residual	Σ speciation	Total (Bulk)	
0_5	0.296	1.208	4.24	4.2	82	91.94	95.47	Under Recovery
5_10	0.456	1.624	4.56	6	99	111.64	116.32	Under Recovery
10_15	0.368	1.456	4.22	5.56	106	117.60	141.80	Under Recovery
15_20	0.68	1.84	4.5	11.82	110	128.84	144.42	Under Recovery
20_25	0.56	1.64	4.9	4.88	113	124.98	140.99	Under Recovery
25_30	2.176	2.608	9.32	10.4	200	224.50	235.75	Under Recovery
30_35	2.432	2.512	7.9	12.16	203	228.00	231.50	Under Recovery
35_40	7.072	3.192	3.76	23.74	196	233.76	244.38	Under Recovery
avearge	**1.755**	**2.01**	**5.425**	**9.845**	**138.625**	**157.66**	**168.83**	